# THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR

Volume X, No. 4

(July-August)

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU
152 West 42nd St., New York 18, N.Y.

—An agency for the interpretation of international knowledge—

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE USSR (ZHURNAL ANALITICHESKOI KHIMII)

July-August, 1950

TABLE OF CONTENTS

| | | |
|---|---|---|
| | English | Russian |
| 1. A Study of the Reaction of Ultra Violet Absorbing Substances. Part II. A. P. Terentiev | 195 | 195 |
| 2. Organic Coprecipitants. 8. Coprecipitation of Thallium. V. I. Nazarenko and K. B. Yatsimirskii | 207 | 207 |
| 3. The Use of Sodium Arsine Agents for Separation of Coprecipitated Arsenic from Sodium Pertechnetate. M. A. Bezborodov | 213 | 213 |
| 4. Coprecipitation of Thallium with Mercury as the Tetraiodomercurate. Thallous Chloride. N. T. Vasilenko | 219 | 219 |
| 5. The Analytical Chemistry of Rhenium. P. I. Nikolaeva and A. I. Lukyan | 225 | 225 |
| 6. Investigation of Complex Compounds of the Dimethyl Ether of Dimercaptoethane in Analytical Chemistry. 1. M. V. Babko and T. A. Tikhon | 231 | 231 |
| 7. Amperometric Study of the Precipitation Titration of Silver Nanogramatic. G. A. Tikhon | 241 | 241 |
| 8. The Use of Some of Silver-Organic Compounds in Ultra Violet Analysis. A. P. Terentiev and M. S. Tsvetkov | 247 | 247 |
| 9. A Rapid Iodo-Spectrophotometric Method for Isotopic Analysis of Oxygen in Water. A. I. Brodskii, S. G. Tsarapkina, L. I. Gribova, and T. S. Andreeva | 253 | 253 |

BRIEF COMMUNICATIONS

| | | |
|---|---|---|
| 10. A Cell For Continuous Infrared Spectral Analysis, and an Apparatus for Measuring the Thickness and the Weight of Cells. L. V. Peshkin and G. S. Landsberg | 261 | 261 |

THE JOURNAL OF ANALYTICAL CHEMISTRY OF THE U.S.S.R.

Volume X (1955)

Number 4 (July-August)

(A Publication of the Academy of Sciences of the U.S.S.R.)

IN ENGLISH TRANSLATION

Copyright, 1955

CONSULTANTS BUREAU

259 West 14th Street

New York 11, N.Y.

Annual subscription $80.00

Printed in the United States Single issue 20.00

Note: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any paper in this issue may be purchased from the publisher for $7.50.

BLANK
PAGE

# A STUDY OF THE BEHAVIOR OF ULTRA SMALL AMOUNTS OF ELEMENTS

## PART I

A. K. Lavrukhina

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry Acad. Sci. USSR, Moscow

The chemistry of low concentrations is a very interesting field of study. The behavior of elements at ultra-low concentrations during various chemical operations – precipitation, electrolysis, extraction, distillation, etc. – has long been of interest to research workers. At present, in view of the numerous radiochemical studies made of the products of various nuclear transformations and the study of the chemical properties of new elements obtained in ultra-small amounts, as the result of nuclear reactions, this question has become of essential importance. This question has been studied right from the time of the discovery of the natural radioactive elements, when the possibility of studying very small concentrations of elements became apparent. Nevertheless, these studies, at that time, were limited to a small number of chemical elements (radium, lead, bismuth, polonium, etc.). Neither could radioactive indicators prepared artificially be used for this purpose, because the activity of the preparations was insufficient. Only recently therefore, as a result of improved methods of preparing various bombarding particles, and of improvements of radiochemical analysis, has it become possible to get radio-isotopes of many chemical elements without carriers.

Radioactive preparations are said to be free of carriers, when, during the course of their isolation, no isotopic carriers are added to them and when the preparations do not contain carriers in amounts detectable by ordinary chemical or spectrographic methods. Carrier free radioactive isotopes contain a very small amount of material. Thus, 1 $\mu$ Cu (Curies) of the $Bi^{210}$ radio-isotope contains $2.5 \cdot 10^{10}$ atoms of bismuth, or $8.6 \cdot 10^{-12}$ g; $Mn^{56}$ $2.0 \cdot 10^{9}$ atoms or $1.9 \cdot 10^{-13}$ g [1]. Since radiometric measurements permit one to measure activities of the order of 0.01 $\mu$ Cu with reasonable accuracy, in practice therefore we can study $10^{-15}$ g of material. Consequently by studying the behavior of the radio-isotopes of various elements, we can get some information on the behavior of these elements at ultra-low concentrations.

During 1953-54 we studied the behavior of elements at ultra-low concentrations during precipitation, extraction, electrolysis, distillation and ion-exchange chromatographic separation. The radioactive isotopes listed in Table 1 were used for this purpose.

These radio-isotopes were given a preliminary purification from contaminating radio-isotopes and were identified by their half-life periods and their $\beta$-ray activity.

The radioactivity of the preparations was measured on a TM-20 torsion counter using a type "B" counter set-up. The time of measurement of the activity was varied so that the statistical error of the counter was < 5%.

Preparation of the targets for measurement of the activity of the precipitates or solutions was carried out as follows:

1) For a low activity, the precipitate (or solution) was completely transferred to a glass target with a diameter of ~20 mm, and dried under a lamp or in a drying oven at 110°.

2) For high activities the precipitate was dissolved in a suitable solvent. The solution obtained was diluted with water to a known volume. An aliquot of the solution was then transferred by means of a micro-pipet graduated in 0.001 ml to a 20 x 25 mm target of tracing cloth. The solution was then evaporated by the method described above.

The activities of such targets were then compared with the activity of a standard solution of the test radio-isotope prepared in the same way as the target measured. All the results quoted in this paper are the means of 6-12 replicates.

TABLE 1

| Radio-isotopes used | Half-life period in days | β-radiation activity in Mev |
|---|---|---|
| $Bi^{210}$ | 5 | 1.17 |
| $I^{131}$ | 8 | 0.25 (14%); 0.6 (86%) |
| $Zr^{95}$ | 65 | 0.4 |
| $Y^{91}$ | 57 | 1.46 |
| $Ce^{141}$ | 30 | 0.6 |
| $Ce^{143}$ | 1.4 | 1.3 |
| $Ce^{144}$ | 280 | 0.3 |
| $Fe^{59}$ | 45 | 0.43 |
| $P^{32}$ | 14.3 | 1.7 |
| $As^{76}$ | 1 | 0.48 (5%); 1.76 (12%) 2.4 (33%); 2.9 (52%) |
| $Co^{60}$ | 4.95 g | 0.3 |
| $Sb^{124}$ | 60 | 0.48 (18%); 0.65 (44%) 1.0 (3%); 1.6 (8%); 2.4 (21%) |
| $Zn^{65}$ | 250 | 0.32 |
| $Nd^{147}$ | 12 | 0.4 (25%); 0.6 (15%); 0.82 (60%) |

We shall now discuss the results of such studies of the behavior of the radio-isotopes of various elements in the analytical operations enumerated above.

## Coprecipitation

Of great importance during various studies is the coprecipitation of radio isotopes with various precipitates deposited from solution. At present, the following types of coprecipitation have been established [2]: isomorphous coprecipitation, adsorption coprecipitation, and formation of irregular mixed crystals and internal adsorption in micro-cracks and micro-capillaries which penetrate the crystals. The most common are the first two types.

Isomorphous coprecipitation has been studied in detail by Khlopin and coworkers [3-9]. As a result of the large amount of work they carried out, they established the well known quantitative relations between the distribution of the micro-element between solid and liquid phases, embracing all the cases of isomorphous coprecipitation, by means of which it is possible to establish the chemical composition of compounds of the element when present in ultra-small amounts.

Adsorption coprecipitation of radio-isotopes by various precipitates is determined by the following factors [4]:

1) By the charge on the surface of the precipitate. Thus, radio-isotopes are effectively adsorbed by precipitates only when the sign of the charge on the surface of the precipitate is opposite to that of the charged ions of the radio-isotope.

2) By the solubility of the compound being adsorbed. Results of our work on the radio-isotope $I^{131}$ and of Ratner's work [10] on $Pb^{212}$ adduced in Table 2, show that with decreasing solubility of the respective compound of the radio-isotope, its adsorption by the precipitate decreases. The solubility of the adsorbent does not affect the adsorption of the radio-isotopes.

TABLE 2

| Precipitate | Its solubility in mole/liter | Radio-isotope | Solubility of the respective compound of the radio-isotope in mole/liter | % adsorption |
|---|---|---|---|---|
| AgBr | $6 \cdot 10^{-7}$ | $Pb^{212}$ | $1 \cdot 10^{-2}$ | 1.8 |
| AgI | $1 \cdot 10^{-9}$ | $Pb^{212}$ | $1 \cdot 10^{-3}$ | 2.1 |
| $Ag_2CrO_4$ | $7 \cdot 10^{-5}$ | $Pb^{212}$ | $1 \cdot 10^{-7}$ | 98 |
| $PbBr_2$ | $1 \cdot 10^{-2}$ | $I^{131}$ | $1 \cdot 10^{-3}$ | 23 |
| AgBr | $6 \cdot 10^{-7}$ | $I^{131}$ | $1 \cdot 10^{-9}$ | 99 |
| HgBr | $3 \cdot 10^{-8}$ | $I^{131}$ | $2 \cdot 10^{-10}$ | 99 |

3) By the value of the surface area of the precipitate. Thus, the greater the surface area of the precipitate, the greater the amount of radio-isotope adsorbed. E.g. calcium sulfate precipitated as coarse crystals does not attract radium from solution, while a fine crystalline precipitate of calcium sulfate adsorbs it completely [4].

Adsorption of radio-isotopes by precipitates is very widespread. All precipitates, independently of their chemical nature, contain various amounts of adsorbed radio-isotopes.

Coprecipitation of radio-isotopes with various precipitates can be lowered, as our experiments showed, by increasing the acidity of the solution. This is evident from the results given in Table 3.

TABLE 3

| Radio-isotopes | Acid concentration in N | Precipitate composition | % Precipitation | Literature cited |
|---|---|---|---|---|
| $Bi^{210}$ | 0.3 | $BaSO_4$ | 98 | Author's results |
| $Bi^{210}$ | 2.0 | $BaSO_4$ | 4 | Author's results |
| $Pb^{212}$ | 0.003 | $AgIO_3$ | 20.7 | [10] |
| $Pb^{212}$ | 0.1 | $AgIO_3$ | 4.4 | [10] |
| $Pb^{212}$ | 0.4 | AgBr | 40 | [11] |
| $Pb^{212}$ | 1.8 | AgBr | 10.5 | [11] |

Coprecipitation of radio-isotopes is lowered by reprecitation of the precipitate and the addition of complexing agents. We have studied the effect of complexing agents on the extent of coprecipitation of radio-isotopes using the coprecipitation of $Bi^{210}$ with AgI as an example. In these experiments 10 mg of $I^-$ was added to 10 ml of a 10% (by volume) solution of nitric acid, this was followed by addition of various amounts of the radio-isotope $Bi^{210}$ (from 10 to $10^{-9}$ mg); 10 mg of $Ag^+$ was finally added. The AgI precipitate formed was centrifuged, washed 3 times with 3% nitric acid and its activity determined.

The results of these experiments showed that in the presence of 10 mg of bismuth, 59% of the $Bi^{210}$ is precipitated with the AgI, on lowering the bismuth concentrations to $10^{-2}$ mg and lower, the amount of bismuth coprecipitated was found to be only 2%. It follows from these results that by decreasing the concentration of the ion, its capacity to form a complex increases under the given conditions; this leads to a decrease in coprecipitation of the given element with the precipitate which separates out from solution.

## Study of the Coprecipitation of Radio-isotopes with Hydroxides and Sulfides

We made a detailed study of the coprecipitation of radio-isotopes with the precipitates of the hydroxides and sulfides of various elements, which are widely used in radiochemical studies and for the concentration of traces of elements.

Coprecipitation with hydroxides and sulfides has been used for a long time in the practice of analytical chemistry for the concentration of small amounts of elements. Nevertheless, up to the present, there has been no unanimous agreement on the views advanced to explain coprecipitation. In this connection, therefore, a study of this question is not only important for analytical and radio-chemical practice, but is also important from the point of view of developing a theory of coprecipitation. The following method was used for the study of coprecipitation with hydroxides.

To a weak acid solution were added solutions of the respective radio-isotopes and the carrier; these additions were followed by addition of a 10% solution of NaOH or $NH_4OH$ till a definite pH established by an indicator was attained. The hydroxide precipitates were centrifuged 30 minutes after precipitation, washed a few times with a 1% solution of NaOH or $NH_4OH$ and dissolved in a few mls of concentrated hydrochloric acid. The solution was diluted with water to 50 ml and the activity of an aliquot determined.

The following conclusions can be drawn from the results adduced in Table 4.

1) Coprecipitation of radio-isotopes with the hydroxides of various metals does not depend on the molar solubility of the latter. E.g., coprecipitation of $Bi^{210}$ with $Fe(OH)_3$ ($S = 3.4 \cdot 10^{-10}$ mole/liter) and with $Fe(OH)_2$ ($S = 1.3 \cdot 10^{-5}$ mole/liter) is 96-98%.

2) The extent of coprecipitation is determined by the solubility of the hydroxide of the radio-isotope of the given element. Thus, its coprecipitation approximates to 100% when the hydroxide is slightly soluble ($S \leq 10^{-4}$ mole/liter), but is very small (from zero to a few percent) when the solubility of the hydroxide is high.

3) Coprecipitation of the radio-isotopes of elements forming slightly soluble hydroxides changes to only an insignificant extent on reprecipitation of the hydroxide; reprecipitation decreases coprecipitation of the radio-isotopes of elements not forming insoluble hydroxides to a considerable extent.

These conclusions re coprecipitation of radio-isotopes with hydroxides of various metals are confirmed by the results of other research workers whose articles are referred to in Table 5.

It also follows from the results given in Table 4 that:

a) coprecipitation of the radio-isotopes of $Bi^{210}$ with $Fe(OH)_3$ does not depend on the amount of iron introduced into solution within the limits of 0.1 to 10 mg/ml;

b) the extent of coprecipitation of $Bi^{210}$ with the hydroxides of various metals depends to only a small extent on the pH of the solution, within the limits 6.2-10.

TABLE 4

| Radio-isotope | Carrier | Amount of carrier in mg/ml | Precipitant | pH of precipitation | Solubility of precipitate in mole/liter | % precipitation |
|---|---|---|---|---|---|---|
| $Bi^{210}$ | $Bi^{3+}$ | 1 | NaOH | 8.2-10 | $1 \cdot 10^{-8}$ | 99.5 |
| $Bi^{210}$ | $Bi^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $1 \cdot 10^{-8}$ | 99 |
| $Bi^{210}$ | $Fe^{3+}$ | 10 | $NH_4OH$ | 4.4-6.2 | $3.4 \cdot 10^{-10}$ | 100 |
| $Bi^{210}$ | $Fe^{3+}$ | 0.5 | $NH_4OH$ | 4.4-6.2 | $3.4 \cdot 10^{-10}$ | 97 |
| $Bi^{210}$ | $Fe^{3+}$ | 0.1 | $NH_4OH$ | 4.4-6.2 | $3.4 \cdot 10^{-10}$ | 97.5 |
| $Bi^{210}$ | $Fe^{3+}$ | 1 | NaOH | 8.2-10 | $3.4 \cdot 10^{-10}$ | 94 |
| $Bi^{210}$ | $Fe^{3+}$ | 1 | NaOH | 4.4-6.2 | $3.4 \cdot 10^{-10}$ | 96.5 |
| $Bi^{210}$ | $Fe^{2+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $1.3 \cdot 10^{-5}$ | 98 |
| $Bi^{210}$ | $Th^{4+}$ | 1 | NaOH | 4.4-6.2 | $3.6 \cdot 10^{-10}$ | 99.5 |
| $Bi^{210}$ | $Th^{4+}$ | 1 | NaOH | 8.2-10 | $3.6 \cdot 10^{-10}$ | 99.8 |
| $Bi^{210}$ | $Th^{4+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $3.6 \cdot 10^{-10}$ | 94.0 |
| $Bi^{210}$ | $La^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $9.2 \cdot 10^{-6}$ | 96 |
| $Bi^{210}$ | $Cr^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $1.2 \cdot 10^{-5}$ | 97.6 |
| $Bi^{210}$ | $Cd^{2}$ | 1 | NaOH | 4.4-6.2 | $8.5 \cdot 10^{-6}$ | 88 |
| $Bi^{210}$ | $Cd^{2}$ | 1 | NaOH | 8.2-10 | $8.5 \cdot 10^{-6}$ | 89 |
| $Bi^{210}$ | $Cu^{2+}$ | 1 | NaOH | 4.4-6.2 | $5.4 \cdot 10^{-7}$ | 94 |
| $Bi^{210}$ | $Cu^{2+}$ | 1 | NaOH | 8.2-10 | $5.4 \cdot 10^{-7}$ | 96 |
| $Ce^{141} + ^{143}$ | $Ce^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $4 \cdot 10^{-6}$ | 98 |
| $Ce^{141} + ^{143}$ | $Fe^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $3.4 \cdot 10^{-10}$ | 87 |
| $Ce^{141} + ^{143}$ | $La^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $9.2 \cdot 10^{-6}$ | 92 |
| $I^{131}$ | $Fe^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $1.3 \cdot 10^{-5}$ | 1.9 |
| $I^{131}$* | $Fe^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $1.3 \cdot 10^{-5}$ | 0.2 |
| $Bi^{210}$* | $Fe^{3+}$ | 1 | $NH_4OH$ | 4.4-6.2 | $3.4 \cdot 10^{-10}$ | 93 |

*Reprecipitation of precipitates.

TABLE 5

| Radio-isotope | Carrier | Temperature | Precipitation conditions | S of the carrier hydroxide in mole/liter | S of the radio-isotope hydroxide in mole/liter | % precipitation of radio-isotope | Literature cited |
|---|---|---|---|---|---|---|---|
| $Ac^{228}$ | $La(OH)_3$ | ~80° | 99% precipitation of $La^{3+}$ | $9.2 \cdot 10^{-6}$ | | ~100 | [12] |
| $Ac^{228}$ | $Al(OH)_3$ | Ditto | 100% precipitation of $Al^{3+}$ | $< 10^{-4}$ | | ~100 | [13] |
| $Ac^{228}$ | $Fe(OH)_3$ | " | – | $3.4 \cdot 10^{-10}$ | $10^{-4}$ | ~100 | [13] |
| $Ac^{228}$ | $Y(OH)_3$ | " | 100% precipitation of $Y^{3+}$ | $1.8 \cdot 10^{-6}$ | | ~100 | [13] |
| $Ac^{228}$ | $Zr(OH)_4$ | Room | – | $8 \cdot 10^{-11}$ | | 100 | [13] |
| $Ca^{45}$ | $Sc(OH)_3$ | Ditto | Excess $NH_4OH$ | | $2 \cdot 10^{-2}$ | 0 | [12] |
| $Ca^{45}$ | $Fe(OH)_3$ | Ditto | Ditto | $3.4 \cdot 10^{-10}$ | $2 \cdot 10^{-2}$ | 0 | [12] |
| $Cu^{64}$ | $Bi(OH)_3$ | Ditto | 100% precipitation of $Bi^{3+}$ | $5 \cdot 10^{-6}$ | Solution complex | 0 | [14] |
| $Pb^{212}$ | $Fe(OH)_3$ | Ditto | 100% precipitation of $Fe^{3+}$ | $3.4 \cdot 10^{-10}$ | $4.8 \cdot 10^{-6}$ | ~100 | [12] |
| $Mn^{54}$ | $Fe(OH)_3$ | Ditto | 100% precipitation of $Fe^{3+}$ | $3.4 \cdot 10^{-10}$ | $3.1 \cdot 10^{-5}$ | 100 | [15] |
| $Ra^{224}$ | $Th(OH)_4$ | Ditto | – | $3.6 \cdot 10^{-10}$ | Solution | 0 | [12] |
| $Th^{234}$ | $Cu(OH)_2$ | ~80° | 0.02 M 60% precipitation $Cu^{2+}$ pH 5 | $5.4 \cdot 10^{-7}$ | $3.6 \cdot 10^{-10}$ | 97 | [12] |
| $Th^{227}$ | $La(OH)_3$ | Room | 4% $La^{3+}$ precipitation | $9.2 \cdot 10^{-6}$ | $3.6 \cdot 10^{-10}$ | 97 | [12] |
| $Zr^{95}$ | $Fe(OH)_3$ | Ditto | – | $3.4 \cdot 10^{-10}$ | $8 \cdot 10^{-11}$ | ~100 | [16] |
| $Co^{56}$ | $Fe(OH)_3$ | Ditto | Excess $NH_4OH$ | $3.4 \cdot 10^{-10}$ | Solution complex | ~1 | [15] |
| $In^{113}$ | $Fe(OH)_3$ | Ditto | – | $3.10^{-10}$ | | ~100 | [17] |
| $In^{111}$ | $Mg(OH)_3$ | 100° | – | $1.1 \cdot 10^{-10}$ | | ~90 | [18] |
| $Nd^{147}$ | $Ce(OH)_3$ | 100° | Precipitate removed from filtrate after 30 minutes | $4 \cdot 10^{-6}$ | $2.7 \cdot 10^{-6}$ | 92.3 | [19] |
| $Y^{91}$ | $Ce(OH)_3$ | 100° | Ditto | $4.0 \cdot 10^{-6}$ | $1.2 \cdot 10^{-6}$ | 93.4 | [19] |
| $Y^{91}$ | $Y(OH)_3$ | 100° | Ditto | $1.2 \cdot 10^{-6}$ | $1.2 \cdot 10^{-6}$ | 96.2 | [19] |
| $Sr^{89}$ | $Fe(OH)_3$ | Room | – | $3.4 \cdot 10^{-10}$ | | 0 | [20] |
| $Sn^{113}$ | $Fe(OH)_3$ | Room | – | $3.4 \cdot 10^{-10}$ | $7.1 \cdot 10^{-12}$ | ~100 | [12] |

Results of a study of the effect of the conditions under which $Fe(OH)_3$ is precipitated (at a concentration of 1 mg Fe/ml) with ammonia on the amount of $Bi^{210}$ coprecipitated are given in Table 6. It is clear from these results that the extent of coprecipitation of $Bi^{210}$ with $Fe(OH)_3$ is independent of the conditions under which this hydroxide is formed.

The study of the coprecipitation of radio-isotopes with the sulfides of various elements was carried out in a 0.3 N nitric acid solution by the usual method of precipitating sulfides.

TABLE 6

| Precipitation conditions | % Precipitation of $Bi^{210}$ |
|---|---|
| Very rapid precipitation of the $Fe(OH)_3$; the precipitate was not allowed to stand | 99 |
| Very slow precipitation (the $NH_4OH$ was added dropwise in the course of 30 minutes with constant stirring); the precipitate was not allowed to stand | 99 |
| Rapid precipitation, filtration 7 hours after precipitation | 98 |
| Rapid precipitation, precipitate allowed to stand for 4 hours at 100° | 98 |

It follows from the results of these experiments, which are adduced in Table 7, and from published results which are collected together in Table 8, that:

a) radio-isotopes of elements which form insoluble sulfides are completely coprecipitated with the sulfides of other elements; this coprecipitation is independent of the solubility of the latter for a very wide range of their molar solubilities (from $10^{-14}$ to $10^{-27}$ mole/liter);

b) no coprecipitation of radio-isotopes of elements which do not form sulfides was observed.

In the case of small amounts of elements which form sulfides in neutral and alkaline media, as follows from Rudnev's work [23], there was observed a selective coprecipitation of these elements with metal sulfides which are insoluble in 0.3 N acid solution. Thus, a study of the coprecipitation of small amounts of zinc, cobalt, iron, nickel, and manganese, with the sulfides of mercury, copper, cadmium, bismuth, tin, antimony, arsenic, lead, and silver showed selective coprecipitation of zinc with CdS (7%), $SnS_2$ (10%) and of cobalt with $SnS_2$ (17.2%). Coprecipitation was negligible in the remaining cases (< 1%).

TABLE 7

| Radio-isotopes | Carrier | Composition of precipitate | % Coprecipitation of the radio-isotopes | S of the carrier sulfide in mole/liter | S of the radio-isotope sulfide in mole/liter |
|---|---|---|---|---|---|
| $Bi^{210}$ | $Bi^{3+}$ | $Bi_2S_3$ | 99.5 | $2 \cdot 10^{-15}$ | $2 \cdot 10^{-15}$ |
| $Bi^{210}$ | $Cu^{2+}$ | CuS | 98 | $2 \cdot 10^{-19}$ | $2 \cdot 10^{-15}$ |
| $Bi^{210}$ | $Cd^{2+}$ | CdS | 100 | $3 \cdot 10^{-14}$ | $2 \cdot 10^{-15}$ |
| $Bi^{210}$ | $Pb^{2+}$ | PbS | 102 | $3 \cdot 10^{-15}$ | $2 \cdot 10^{-15}$ |
| $Bi^{210}$ | $Hg^{2+}$ | HgS | 100 | $6 \cdot 10^{-27}$ | $2 \cdot 10^{-15}$ |
| $Ce^{141} + 143$ | $Bi^{3+}$ | $Bi_2S_3$ | 0 | $2 \cdot 10^{-15}$ | not formed |
| $Ce^{141} + 143$ + 1 mg/ml of the isotopic carrier | $Bi^{3+}$ | $Bi_2S_3$ | 0 | $2 \cdot 10^{-15}$ | not formed |
| $Zr^{95}$ | $Bi^{3+}$ | $Bi_2S_3$ | 0.8 | $2 \cdot 10^{-15}$ | Zirconium is partially precipitated with the sulfides in the absence of tartaric acid |
| $Zr^{95}$ + 1 mg/ml of isotopic carrier | $Bi^{3+}$ | $Bi_2S_3$ | 2.1 | $2 \cdot 10^{-15}$ | |

On this basis therefore it is possible to conclude that during precipitation of the hydroxides (or sulfides) of any metal, all the radio-isotopes of elements present in the test solution which are capable of forming slightly soluble hydroxides (or sulfides) are precipitated with it. The nature of the carrier is not, therefore, very important.

## SUMMARY

1. During precipitation reactions, radio-isotopes are coprecipitated to varying degrees with the precipitates which separate out. This coprecipitation is complete, when the radio-isotopes form compounds crystallizing isomorphously or isodimorphously with the respective compounds of the macro elements, or when they form slightly soluble compounds with the ion of the precipitate with opposite charge.

TABLE 8

| Radio-isotope | Carrier | Precipitant | Precipitation conditions | S of carrier sulfide in mole/liter | S of radio-isotope sulfide mole/liter | % coprecipitation | Literature cited |
|---|---|---|---|---|---|---|---|
| $Cu^{64}$ | $Bi_2S_3$ | | $Zn^{2+}$, $H^+$, $SO_4^{2-}$ | $2\cdot10^{-15}$ | $2\cdot10^{-19}$ | 100 | [14] |
| Ga? | CdS | $H_2S$ | – | $3\cdot10^{-14}$ | not precipitated | 0 | [16] |
| Ga? | AgS | $H_2S$ | – | $6\cdot10^{-18}$ | not precipitated | 0 | [16] |
| Ga? | CuS | $H_2S$ | – | $2\cdot10^{-19}$ | not precipitated | 0 | [16] |
| $Pb^{210}$ | $Bi_2S$ | $(NH_4)_2S$ | – | $2\cdot10^{-15}$ | $3\cdot10^{-15}$ | ~100 | [20] |
| $Pb^{210}$ | FeS | $H_2S$ | Neutral solution | $2\cdot10^{-10}$ | $3\cdot10^{-15}$ | ~100 | [12] |
| $Pb^{210}$ | HgS | $H_2S$ | 0.02 $MH^+$ | $6\cdot10^{-27}$ | $3\cdot10^{-15}$ | ~100 | [12] |
| $Pb^{210}$ | CuS | $H_2S$ | Ditto | $2\cdot10^{-19}$ | $3\cdot10^{-15}$ | ~100 | [14] |
| Tl? | $As_2S_3$ | $H_2S$ | 10 M HCl, 24 hrs. standing | $4\cdot10^{-29}$ | not precipitated | 0 | [22] |
| $Tl^{234}$ | FeS | $FeCl_3$ | $(NH_4)_2CO_3$, $NH_4Cl$, $(NH_4)_2S$ | $2\cdot10^{-10}$ | not formed at | 0 | [21] |
| $Bi^{210}$ | CuS | $H_2S$ | 0.02 M $H^+$ | $2\cdot10^{-19}$ | $2\cdot10^{-15}$ | ~100 | [12] |
| $Bi^{210}$ | HgS | $H_2S$ | 0.02 M $H^+$ | $6\cdot10^{-27}$ | $2\cdot10^{-15}$ | ~100 | [12] |
| $Ac^{227}$ | $Bi_2S_3$ | $H_2S$ | acid solution | $2\cdot10^{-15}$ | not formed | 0 | [12] |
| $Ac^{227}$ | CuS | $H_2S$ | Ditto | $2\cdot10^{-19}$ | Ditto | 0 | [12] |
| $Ac^{227}$ | PbS | $H_2S$ | Ditto | $3\cdot10^{-15}$ | Ditto | 0 | [12] |
| $Cm^{242}$ | $In_2S_3$ | $H_2S$ | Precipitation from acetic acid solution | | Ditto | 0 | [12] |
| $Po^{210}$ | $Bi_2S_3$ | $H_2S$ | 1 M HCl, 30 minutes 50% $Bi^{3+}$ precipitated | $2\cdot10^{-15}$ | – | 96 | [12] |
| $Po^{210}$ | CuS | $H_2S$ | 1 M HCl, 24 hours 40% Cu precipitated | $2\cdot10^{-19}$ | – | 94 | |
| $Fr^{223}$ | PbS | $H_2S$ | From neutral solution | $3\cdot10^{-15}$ | not formed | 0 | |
| Tc? | CdS | $H_2S$ | 0.24 M HCl | $3\cdot10^{-12}$ | – | ~100 | [22] |
| Tc? | CuS | $H_2S$ | 1.2 M HCl | $2\cdot10^{-19}$ | – | ~100 | [22] |
| Tc? | $Re_2S_7$ | $H_2S$ | 0.24-5 M HCl, 24 hrs. standing | | – | ~100 | [22] |

In the remaining cases coprecipitation of the radio-isotopes is incomplete. Coprecipitation can be lowered by reprecipitation, by making the medium sufficiently acid, or by adding complexing agents.

2. Coprecipitation of radio-isotopes with the hydroxides and sulfides of various metals is independent of the molar solubility of the latter, and is determined solely by the value of the molar solubility of the respective compound of the radio-isotope. Coprecipitation of radio-isotopes of elements forming insoluble hydroxides is practically independent of the conditions employed for precipitating the hydroxide.

Received April 29, 1955

## LITERATURE CITED

[1] E. Brode, "The Present State of Radiochemistry" Foreign Literature Press, 1952, p. 11.

[2] S. Bresler, "Radioactive Elements", State Theor.-Tech. Press, 1952, p. 105.

[3] V. Khlopin, Proc. Acad. Sci. USSR, 101 (1924).

[4] V. Khlopin, and M. Merkulova, "Radiochemistry, Collected Papers" IMU. p. 115.

[5] V. Khlopin, Trans. State Radium Institute 4, 34 (1938).

[6] V. Khlopin, and P. Tolmachev, Bull. Acad. Sci. USSR, Div. Metl.Eng. Sci., 43 (1932).

[7] V. Khlopin, and A. Ratner, Proc. Acad. Sci. USSR (A) 723 (1930).

[8] V. Khlopin, and V. Klokman, Bull. Acad. Sci. USSR, Div. Chem. Sci. 254 (1949); Proc. Acad. Sci. USSR, 70, 45 (1949).

[9] V. Khlopin, Proc. Acad. Sci. USSR, 71, 901 (1950).

[10] A. Ratner, "Radioactive Indicators and Their Uses", Leningrad 1936.

[11] O. Hahn, "Applied Radiochemistry", State Chem. Press, Moscow-Leningrad, (Translation) 1947, 157.

[12] A. Wahl, N. Bonner, Radioactivity Applied to Chemistry, New York-London (1951) p. 142.

[13] D. Yovanovitch, J. chim. phys. 23, 1 (1926).

[14] H. Born, U. Drehmann, Naturwissenschaften 32, 159 (1945).

[15] R. Maxwell, J. Gile, W. Garrison, J. Hamilton, J. Chem. Phys., 17, 340 (1949).

[16] O. Hahn, F. Strassmann, W. Seelmann-Eggeberg, Z. Naturforsch, 1, 545 (1946).

[17] R. Maxwell, H. Haymond, D. Bomberger, W. Garrison, J. Hamilton, J. Chem. Phys., 17, 1005 (1949).

[18] E. Jacobi, Helv. Phys. Acta, 22, 66 (1949).

[19] L. Gerhardt, Naturwissenschaften, 33, 24 (1946).

[20] A. Fleck, J. Chem. Soc. 1913. 103, 1052.

[21] M. Bachelet, Comptes rend, 203, 69 (1936).

[22] C. Oarrier, E. Segre, J. Chem. Phys. 7, 155 (1939).

[23] N. Rudnev, J. Anal. Chem., 8, 3, (1953) (T. P. 1) *.

* T. P. = C. B. Translation pagination.

BLANK
PAGE

# ORGANIC COPRECIPITANTS

## 3. COPRECIPITATION OF THALLIUM

V. I. Kuznetsov and G. V. Myasoedova

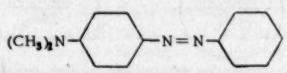
The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry Acad. Sci., USSR, Moscow

In recent years the chemistry of thallium has been receiving increasing attention. A comparative study has been made of the reactions used for detecting thallium [1], a number of reviews have been devoted to the method of determining it [2, 3], and new, sensitive methods have been described for its detection and determination [4, 5, 6]. The new technique of radiochemical analysis has been used for its determination [7, 8]. Determination of small amounts of thallium is of interest from the viewpoint of geochemistry [9], biological sciences [10], and other branches of science.

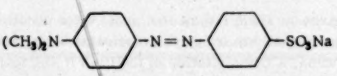
The possibility of coprecipitating thallium with organic coprecipitants has been pointed out by us before [11]. We also noted at the same time that its organic analog, diphenyliodonium $(C_6H_5)_2I^+$, whose precipitation reactions are very similar to those of thallium [12], is unsuitable for coprecipitating thallium.

Coprecipitation of thallium with organic precipitants is connected with a strongly expressed tendency of the halide complex-anions of trivalent thallium to form slightly soluble salts with heavy organic cations on which many methods of detecting and determining thallium are based [4, 5, 7, 13, 14, 15].

As noted previously [11], if thallium is converted beforehand into $TlCl_4^-$, its coprecipitation can be carried out with the precipitate formed by means of p-dimethylaminoazobenzene



and sodium p-dimethylaminoazobenzene-p'-sulfonate (methylorange).



These ingredients of the precipitant were selected as the result of tests on a number of compounds. Methylviolet, which is very suitable in other cases, is not quite so suitable for coprecipitating thallium, possibly as a result of the strong oxidizing action of the $TlCl_4^-$ anion.

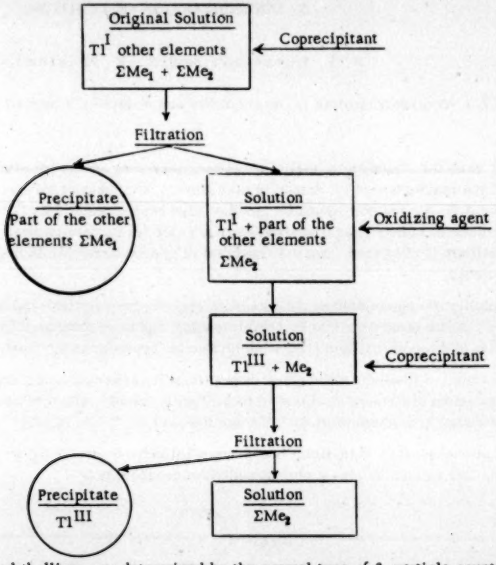
Coprecipitation of thallium with these ingredients is complete but is not selective. Antimony is attracted into the precipitate if it is present as the anion $SbCl_6^-$, so is gold ($AuCl_4^-$), and also molybdenum and tungsten, particularly if they are present as the heteropoly acids. Iron is partially trapped ($Fe^{III}$). It is possible, however, to carry out coprecipitation of thallium practically free from all elements, if use is made of the fact that univalent thallium is not coprecipitated by this same coprecipitant, so that all the other elements which can be precipitated with this coprecipitant are removed beforehand, leaving univalent thallium in solution. The technique employed is shown schematically in the diagram.

### Coprecipitation of Thallium from Pure Solutions

For a study of thallium coprecipitation, the radio-isotope used was $Tl^{204}$, which is a $\beta$-ray emitter with a particle energy of 0.8 Mev and a half life period of 2.7 years.

Thallium was coprecipitated as follows. To a solution of Tl as $TlNO_3$ with the Tl as $Tl^{204}$ in 0.2 N HCl, was

added a filtered solution of bleaching powder* and the mixture left for one hour. The components of the coprecipitant were then added with careful stirring. A dark brown precipitate was formed. After standing for half an hour the precipitate was filtered, washed, dried, and transferred to a porcelain crucible. It was there wetted with sulfuric acid and then heated; it was finally washed in a muffle at a temperature not exceeding 400°. Details of the method are given later on in this article.




The amount of coprecipitated thallium was determined by the normal type of β-particle counter by the number of impulses. The amount of $Tl^{204}$ used for each test gave 1200-1600 impulses/minute, the background amounted to 20-40 impulses/minute.

Results of these tests which are given in Table 1 show that under these conditions, even at a dilution of thallium of $1:1\cdot10^{10}$, complete coprecipitation of thallium occurs. This indicates a very favorable partition coefficient of thallium between precipitate and solution. Coprecipitation of thallium from more dilute solution was not studied, since at higher dilutions the reliability of the estimation of dilution falls off rapidly, because of the possibility of traces of thallium being present in the products employed.

Other experiments whose results are not given in this paper showed that complete coprecipitation occurs from solutions of 0.2-2 N HCl.

TABLE 1

Coprecipitation of Thallium from Dilute Solutions in 0.2 N HCl

| Thallium Dilution | % Coprecipitated | Thallium Dilution | % Coprecipitated |
|---|---|---|---|
| $1:2\cdot10^{7}$ | 89 | $1:1\cdot10^{9}$ | 90 |
| $1:5\cdot10^{7}$ | 90 | $1:3\cdot10^{9}$ | 106 |
| $1:1\cdot10^{8}$ | 91 | $1:5\cdot10^{9}$ | 98 |
| $1:2\cdot10^{8}$ | 92 | $1:1\cdot10^{10}$ | 93 |
| $1:5\cdot10^{8}$ | 105 | | |

* The authors successfully used the technical product. Thallium could not be detected in this product even after concentration of any possible thallium by the method described.

## Coprecipitation of Thallium and its Separation from Other Elements

Of the common elements, the only one which gave any trouble when the above technique was employed, was iron.

Using the values given for the normal potentials for the system

$$Fe^{III}/Fe^{II} = 0.77 \text{ V and}$$
$$Tl^{III}/Tl^{I} = 1.22 \text{ V [16]}$$

and when working in a sufficiently acid medium (0.2 N HCl; pH 0.7), it would appear that the equilibrium reaction

$$2Fe^{III} + Tl^{I} \rightleftharpoons 2Fe^{II} + Tl^{III}$$

should be practically completely shifted to the left. Elementary calculation using Nernst's equation

$$E = E_0 + \frac{0.058}{n} \log \frac{\text{oxidation}}{\text{reduction}}$$

shows that to ensure that 99.9% of the thallium is present in the univalent state ($E_{system} = 1.16$ V) it is enough for only $1.7 \cdot 10^{-7}$ part of the trivalent iron present to be converted into the divalent state.

In actual fact however, as was shown experimentally, it is necessary to have practically all the iron present in a divalent form in order to ensure that the thallium is present in the unprecipitable univalent state. Under such conditions, the above mentioned equilibrium is seen clearly to be established at a slow rate in hydrochloric acid solutions at room temperature.* A freshly prepared mixture of $Tl^{I}$ and $Fe^{III}$, kept at room temperature only starts to give a reaction for $Tl^{III}$ after many hours standing. However only a short period of heating to the boil is sufficient to cause the mixture to give a reaction for $Tl^{III}$ ($TlCl_4^-$ with methylviolet [13]).

During the first precipitation of the unwanted elements, it is necessary in order to ensure that the thallium is present in the unprecipitable univalent state to use a strong reducing agent (hydroquinone). This, however, converts almost all the iron present into divalent iron which is not precipitated during the first precipitation. In the subsequent stages this iron oxidized to $Fe^{III}$ is partially coprecipitated with thallium, so that it becomes essential, either to reprecipitate the thallium in order to get rid of the iron, or use some other method for removing the iron. Thallium may be separated, from iron for example, by hydrolytic precipitation of ferric hydroxide by heating with urea. As a consequence of the difference in hydrolyzability between $Fe^{III}$ and $Tl^{III}$ [18], and of the fact that only a small amount of thallium is trapped by ferric hydroxide, such a method can be used for the separation of thallium from a large amount of iron.**

Separation is effected as follows: to the solution containing the thallium and iron ($Fe^{III}$) in 0.2 N HCl, urea is added in small amounts until the solution becomes turbid. The solution is then heated on a water bath for one hour, the precipitate is filtered, washed with 1% $NH_4Cl$, dissolved in HCl and the ferric hydroxide precipitated again by addition of urea.

For a ratio of thallium to iron in the original solution of $1 : 10^6$ 91% of the thallium added (0.15 γ thallium, 150 mg iron, original volume 300 ml) was removed from the filtrate after one precipitation.

Separation of thallium from other elements present presents no difficulty.

The method recommended for the coprecipitation of thallium can be used for preliminary separation and concentration of thallium during the determination of very small amounts of thallium in various objects.

Table 2 contains some results of determinations of thallium in synthetic mixtures, while Table 3 contains results on the determination of thallium in granite contaminated with it. Determinations were carried out by the technique described below, using radioactive $Tl^{204}$.

Contamination of granite was effected by pouring 0.5 –1 ml of a solution of thallium nitrate containing $Tl^{204}$ in the finely ground granite (1-5 g) and the powder dried. This treatment was carried out in a platinum crucible; the granite was broken down with hydrogen fluoride. Decomposition of the granite by fuming with soda leads to a

* Ashurst and Higginson [17], studied the reaction kinetics between $Fe^{2+}$ and $Tl^{3+}$ in $HClO_4$ solutions.

** T. Moeller and G. H. King [18], also note the possibility of separating iron and thallium by an acetate variant; this method however does not give a clean-cut separation either.

TABLE 2

Determination of Thallium in Synthetic Mixtures Corresponding in Composition to Granite. Volume of Solution 100 ml. Elements added to the solution in each test, calculated as the oxide in mg: $SiO_2$ – 71, $Al_2O_3$ – 16, MgO – 1, $Fe_2O_3$ – 2, CaO – 2, $Na_2O$ – 3, $K_2O$ – 5.

| Ratio of thallium to the sum of the other elements | Thallium dilution in the original solution | Thallium | | | |
|---|---|---|---|---|---|
| | | Taken in γ | Found in γ | Taken in % | Found in % |
| $1:1\cdot10^6$ | $1:1\cdot10^9$ | 0.10 | 0.10 | 0.0001 | 0.0001 |
| $1:1\cdot10^5$ | $1:1\cdot10^8$ | 1.00 | 1.00 | 0.001 | 0.001 |
| 1:200 | $1:2\cdot10^6$ | 50.0 | 40.0 | 0.05 | 0.04 |
| 1:100 | $1:1\cdot10^5$ | 1000 | 900 | 1.00 | 0.90 |

TABLE 3

Determination of Thallium in Granite Contaminated with Thallium. Weight of Granite in Test 1, 5 g; in other tests, 1 g.

| Number of test | Thallium added in γ | Thallium as % of the granite to which it is added | Thallium found as % of that added |
|---|---|---|---|
| 1 | 0.05 | 0.000001 | 91 |
| 2 | 0.1 | 0.00001 | 90 |
| 3 | 1.0 | 0.0001 | 89 |
| 4 | 10.0 | 0.001 | 92 |
| 5 | 100 | 0.01 | 95 |
| 6 | 1000 | 0.1 | 94 |

loss of thallium because of its volatility (data about the volatility of thallium will be communicated in a further article).

The apparent incomplete coprecipitation of thallium may be caused by screening of the $Tl^{204}$ radiation, for which no correction was applied.

A Method for Coprecipitation of Thallium and its Separation From Other Elements (Applicable to Granite and Other Silicate Rocks)

The following special solutions are necessary:

1) A filtered solution of bleaching powder: 30 g of bleaching powder is macerated with 100 ml of water for 10 minutes and the solution filtered.

2) A solution of p-dimethylaminoazobenzene hydrochloride: 6 g of p-dimethylaminoazobenzene is dissolved with gentle heating in 97 ml of ethyl alcohol to which has been added 3 ml of concentrated hydrochloric acid.

3) A saturated aqueous solution of sodium p-dimethylaminoazobenzene-p'-sulfonate (Methylorange).

4) Wash liquor: to 150 ml of water is added 5 ml of 6 N HCl and 0.5 ml each of solutions (2) and (3).

1.5 g of finely ground granite is moistened in a platinum crucible with a few drops of water and 0.5 ml of concentrated sulfuric acid and 5 ml of hydrogen fluoride added; the mixture is evaporated first on a water bath and then on a sand bath till a dry residue is obtained. This treatment is repeated 2-3 times. 5 ml of hydrogen chloride (sp.gr.1.12) is added to the dry residue and the mixture heated again on a water bath and then transferred to a 50 ml beaker, the crucible being washed out with 10 ml of hot hydrogen chloride (sp.gr.1.12). 20-50 mg of solid hydroquinone is added to the hydrochloric acid solution, the beaker covered with a watch glass and the beaker and its contents heated on a water bath for one hour. The solution is transferred to a liter beaker and 250-300 ml of water added to bring the concentration of the hydrochloric acid to 0.2-0.3 N. To the solution obtained, without heeding any precipitate which may be present, is added 20 ml of the p-dimethylaminoazobenzene solution, the whole is stirred, and while still stirring 20 ml of Methylorange solution added slowly, dropwise. After 30-40 minutes, the dark brown precipitate which separates out is filtered through a filter paper (white ribbon quality) and washed with 40-80 ml of wash liquor. To oxidize $Tl^{I}$ to $Tl^{III}$, the solution of bleaching powder is added to the filtrate until the color changes to yellow, which indicates that sufficient oxidizing agent is present; this solution is left for one hour and given a stir now and again. 25 ml of p-dimethylaminoazobenzene is then added to this solution, the whole mixed, and a further 25 ml of Methylorange solution added as before, slowly, dropwise, with thorough agitation all the time.

After 30-40 minutes, the precipitate which separates out is filtered through a filter paper, washed with 40-80 ml of wash liquor, dried, and transferred on the filter paper to a porcelain crucible; it is then wetted with 0.5 ml of diluted (1:1) sulfuric acid and carbonized under an infra-red lamp. The crucible plus carbonized precipitate is placed in a cold muffle, the current switched on and the temperature raised slowly over 3-4 hours to 350-400°, at which temperature it is maintained until washing is complete; using the amount of coprecipitant recommended, this should be 1.5-2 hours.

Coprecipitated thallium remains in the residue which may also contain small amounts of iron and very small amounts of other elements.

## SUMMARY

Thallium converted into the $TlCl_4^-$ anion can be completely coprecipitated even from its very dilute solutions in 0.2 N hydrochloric acid with the precipitate formed by p-dimethylaminoazobenzene and sodium p-dimethylaminoazobenzene-p'-sulfonate (Methylorange).

Quantitative coprecipitation occurs at dilutions of thallium of $1:1 \cdot 10^{10}$.

Thallium can be separated beforehand from other elements by having the thallium in solution as $Tl^{I}$, in which state thallium is not coprecipitated while all the other elements are. The $Tl^{I}$ in the filtrate from the first precipitation is then oxidized to $Tl^{III}$ with bleaching powder and is then coprecipitated in this form with further separation from the other elements.

A method is described for isolating thallium from granite when the latter contains $0.1\text{-}1.10^{-6}$ % of thallium.

Received April 25, 1955

## LITERATURE CITED

[1] P. Wenger, R. Duckert, Y. Russoni, Helv. chim. Acta, 26, 338 (1942).

[2] A. Chretien, I. Longi, Bull. Soc. chim., France (5) 11, 241 (1944).

[3] J. R. A. Anderson, Anal. Chem., 25, 108 (1953).

[4] F. Feigl, V. Gentil, D. Goldstein, Anal. chim. Acta, 9, 393 (1953).

[5] H. Yurany, Mikrochemie, 34, 398 (1949).

[6] W. Geilmann, Angew. Chem., 66, 454 (1954).

[7] T. Ishimori, Bull. Chem. Soc. Japan, 26, 336 (1953); Cited in chim. Analitique, 36, 56 (1954).

[8] C. I. Delbecq, L. E. Glendenin, P. H. Yuster, Anal. Chem., 25, 350 (1953).

[9] L. H. Ahrens, Trans. Geol. Soc. South Africa, XLVIII 204 (1946), Translation in the Collection "Rare Elements in Rocks and Minerals". Edited by V. V. Sheherbiny, 1952, Moscow.

[10] P. H. Schultz, Angew. Chem., 65, 599 (1953).

[11] V. I. Kuznetsov, J. Anal. Chem., 9, 199 (1954) (T. p. 221).*

[12] G. M. Schwab, I. Pechlivanidis, Swansk Kem. Tid., 59, 130 (1947).

[13] V. I. Kuznetsov, J. Anal. Chem., 2, 181 (1947).

[14] H. Wachsmuth, C. A., 42, 1526 (1948).

[15] V. I. Kuznetsov, Prog. Chem., 18, 75 (1949).

[16] Yu. Yu. Lure, "Chemists' Handbook". State Chem. Press, Moscow-Leningrad, 1947.

[17] K. G. Ashurst, W. C. E. Higginson, J. Chem. Soc., 3044, Oct. 1953.

[18] T. Moeller, G. L. King, J. Am. Chem. Soc., 75, 4852 (1953, No. 19).

* T. p. = C. B. Translation pagination.

BLANK
PAGE

# THE USE OF SURFACE ACTIVE AGENTS FOR PREVENTION OF COPRECIPITATION OF IONS WITH SULFIDE PRECIPITATES

N. A. Rudnev

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Precipitation of metals by means of hydrogen sulfide for the purpose of quantitative separation often does not lead to satisfactory results, since cations of the third analytical group, which should, according to the experimental conditions used, remain in solution [1, 2], and coprecipitate with the sulfides of the fourth and fifth groups.

Of methods described in the literature, reprecipitation is the technique most often recommended for the most complete separation of the metals. In addition, in order to decrease coprecipitation, the precipitates have been treated with acids and experimental conditions such as the pH of the solution, the temperature of precipitation, rate of saturation with hydrogen sulfide have all been varied. Complexing agents have also been tried [3].

These methods have led to positive results in some cases, but in other cases separation of the metals of the fourth and fifth groups has been incomplete and the results have frequently been unsatisfactory. Nevertheless, there are methods of combating coprecipitation which deserve investigation on a wide scale. Such a method is the use of organic surface active agents. Surface active agents have not yet been used as they should in chemical analysis, although there is no doubt that they have possibilities. By interacting with the sulfide precipitates separating out, they modify their surface properties and prevent coprecipitation. Very little work has been carried out along these lines hitherto.

Caldwell and Moyer [4], used crotonic aldehyde, formaldehyde, and benzaldehyde for prevention of coprecipitation of zinc with cupric sulfide. The first of these aldehydes was found to give the best results since it lowers the extent of zinc coprecipitation strongly.

Flagg [5], while investigating the separation of tin (IV) from cobalt by means of hydrogen sulfide, used acrolein. As the author points out, coprecipitation of this element with $SnS_2$ is very small.

In order to get a zinc sulfide precipitate at room temperature which is easily filtrable, Caldwell and Moyer in an earlier paper [6], recommended the addition of small amounts of gelatin or agar-agar during precipitation.

Figurovsky and Ushakova [7], have studied the influence of various organic materials on the dispersivity and fractional composition of barium sulfate. This study is of interest from the point of view of that it is a study of the process of formation of precipitates and of getting particles of different sizes which are related to the presence of contaminants in them.

We used various organic materials for preventing coprecipitation of metals with sulfides. Metal sulfides which give hydrophobic sols can interact both with hydrophobic and with hydrophilic colloids. This interaction has a characteristic feature, which may show varying effects on the capacity of these two groups of colloidal materials to prevent coprecipitation.

As our experiments showed, dyes which are hydrophobic colloids are of particular interest for preventing coprecipitation. The interaction of basic dyes with sulfides is determined by their positive charge and their surface active properties. In the case of formation of surface active compounds, during reactions between an organic cation and $HS^-$ and $S^{2-}$ ions, and with an adsorbed sulfide sol or gel, suppression of coprecipitation should be clearly expressed.

A study which we made of the sorption isotherm of Neutral red with cadmium sulfide showed that this dye is absorbed almost in equimolar amounts, and that it is practically impossible to get rid of it by washing. These facts indicate that a stable bond exists between Neutral red and the sulfide. It is natural to suppose that its interaction with the negatively charge sulfide sol should give precipitates possessing a minimum capacity to coprecipitate various cations.

Lowering of the coprecipitation with the aid of large organic anions which are readily sorbed by the sulfides may be connected with the substitution of $HS^-$ and $S^{2-}$ ions found on the surface of the precipitate by the large organic

anions. In addition, it is possible that slightly soluble compounds with the metal sulfides are formed, which would also lead to a decrease in coprecipitation.

It is interesting to examine the effect of hydrophilic colloids. It is difficult to assume chemical interaction for this group of substances, nevertheless, their capacity to cover particles of precipitate with adsorbed layers decreases coprecipitation of various metals.

Some aldehydes, particularly unsaturated ones, are very reactive and may interact with the $HS^-$ and $S^{2-}$ ions found on the surface of sulfide precipitates. Thus, this group of materials is also interesting from the point of view of its possible application for preventing coprecipitation of metal ions with sulfides.

In the work described here, we have been studying the effect of surface active materials in preventing coprecipitation of traces of thallium with arsenic sulfide (III), coprecipitation in this case being very marked. The amount of coprecipitated thallium was determined by the method of "marked" atoms, the radio-isotope $Tl^{204}$ being used.

## EXPERIMENTAL

The radio-isotope $Tl^{204}$ ($T/2 = 2.7$ years), used for the determination of the amount of thallium coprecipitated, was carefully purified by a three-fold precipitation with phosphomolybdic acid and then with bismuth nitrate in the presence of potassium iodide. The thallium was then converted into the iodide in order to determine its amount and then into the nitrate; 1 ml contained 14.2 γ thallium, which gave ca. 50,000 impulses/minute.

A 0.1 M solution of $Na_3AsO_3$, was used for tests with arsenic sulfide (III).

The solutions of the dyes and protective colloids were made before the tests. Concentrations used were 0.5% or 0.25% (in the case of ones with low solubility), formaldehyde 40% and salicylaldehyde 100%.

A steady flow of hydrogen sulfide was obtained by the following method. Ferrous sulfide was placed in a 0.5 liter flask. 200 ml of distilled water and 50 ml of HCl (1.19) were added, after which the flask was closed with a rubber bung fitted with two glass tubes, one of which was connected with a "Drechsel" flask for washing the hydrogen sulfide. The end of the second tube was lowered into a 250 ml cylinder containing water. The throughput of hydrogen sulfide was regulated by screwclips on the tube connecting the Drechsel flask to the flask containing the FeS and by lowering the end of the second tube to a definite level in the water cylinder through which the excess hydrogen sulfide passes.

A 0.1 M solution of sodium arsenite, 1 ml of the thallium radio-isotope (14.2 γ), 5.7 N hydrochloric acid and water were introduced into a 150 ml flask to bring the total volume to 100 ml. The amount of $Na_3AsO_3$ measured out was such that the weight of precipitated sulfide amounted to 0.1g, while the hydrochloric acid was 0.3 N. A stirrer was then placed in the solution and hydrogen sulfide passed. In other tests, the contents of the flask were heated beforehand to the boil. The amount and rate at which hydrogen sulfide passed through the flask were varied; a rapid flow for 5 minutes, or 50-60 bubbles in 15 minutes.

After completion of precipitation of the sulfides, the solution and precipitate were transferred from the flask to a centrifuge tube. 10 ml aliquots of the solutions were taken for measurement of the activity. Measurements were carried out on a watch glass 7 cm in diameter, on which had been placed a circle of filter paper 6.5 cm in diameter. After evaporation on a water bath and placing the watch glass on a suitable stage, the activity of the test aliquot was measured on a B-2 set-up.

In those cases where the amount of coprecipitated thallium was < 20%, the sulfide precipitate was washed by decantation 6 times with hydrogen sulfide water containing 0.1% $NH_4Cl$, and dissolved in $HNO_3$ (1.4). The solution obtained was evaporated and its activity determined. In addition, the activity of 10 ml of filtrate from the sulfide was also determined.

In order to check on the accuracy of the technique employed, the relation between activity of the preparation and the number of impulses/minute was determined. To do this, various amounts of thallium were measured out on watch glasses and the activity of these preparations determined. A calibration curve was drawn up on the basis of these results. Tests showed that the method described is suitable for determining the amount of coprecipitated thallium. The results given below are the means of 3-4 replicates.

### Prevention of Coprecipitation of Thallium with Arsenic Sulfide (III)

In the first series of experiments the effect of certain basic dyes of the triphenylmethane group, azines, and azo dyes were tested as well as certain protective colloids and aldehydes on the coprecipitation of thallium with arsenic sulfide (III).

In the tests adduced below precipitation was carried out at ca. 20° with a rapid stream of hydrogen sulfide. The precipitate in the flask was then shaken in a mechanical shaker for 15 minutes. Results are given in Table 1.

TABLE 1

Prevention of Precipitation of Thallium with Arsenic Sulfide (III) by means of Organic Materials. Rapid Saturation with Hydrogen Sulfide at 20°, Amount of $As_2S_3$ 0.1 g; Tl 14.2 γ, HCl 0.3 N

| Number of test | Organic Material | Thallium coprecipitated | |
|---|---|---|---|
| | | in γ | in % |
| 1 | None added | 14 | 99.2 |
| 2 | Neutral red | 13.1 | 92.2 |
| 3 | Malachite green | 12.9 | 90.7 |
| 4 | Methylene blue | 13.5 | 95.3 |
| 5 - 13 | Fuchsin diamond, Rhodamine B, Aniline yellow, gelatin, tannin, starch, saponin, salicylaldehyde, formaldehyde | 13.7-14.0 | 96.2-99.1 |

The results given in Table 1 show that under the conditions employed, Malachite green and Neutral red have some effect on the coprecipitation of thallium with arsenic sulfide.

The effect of the rate of saturation of the solution with $H_2S$ and the temperature of precipitation were studied next. Malachite green, which showed some promise as a coprecipitation suppressor for thallium, was used as the surface active agent. Results are given in Table 2.

A comparison of the results of Tables 1 and 2 permits one to conclude that in the case of coprecipitation of thallium with $As_2S_3$, the rate of saturation with hydrogen sulfide and the temperature are of vital importance if the surface active agent is to be effective.

In view of the important part played by these two factors, the effect of the organic materials adduced in Table 1 on the prevention of coprecipitation for a slow rate of saturation with hydrogen sulfide at a temperature of precipitation of 100° was studied. Results are given in Table 3.

TABLE 2

Prevention of Coprecipitation of Thallium with Arsenic Sulfide (III) by Means of Malachite green. Throughput of Hydrogen Sulfide 50-60 Bubbles/Minute; Temperatures 20 and 100°; Amount of $As_2S_3$ 0.1 g; Tl 14.2 γ; HCl Concentration 0.3 N

| % Thallium coprecipitated at 20° | | % Thallium coprecipitated at 100° | |
|---|---|---|---|
| without Malachite green | with Malachite green | without Malachite green | with Malachite green |
| 99.2 | 69.2 | 91.1 | 2.1 |

The results given in Table 3 show that the most effective of these materials for preventing coprecipitation of thallium with arsenic sulfide are the basic dyes of the triphenylmethane group. Malachite green and brilliant green give particularly complete prevention of coprecipitation of thallium with $As_2S_3$.

The azines Neutral red and Methylene blue strongly depress coprecipitation; suppression is not so marked in the case of Aniline yellow and Rhodamine B.

The protective colloids are not much good, with the exception of gelatin which depresses coprecipitation appreciably. The aldehydes tested were even less effective as coprecipitation suppressors. The part played by temperature is an interesting one since its effect may be different for $As_2S_3$ which is X-ray amorphous, and for sulfides which have a crystalline structure.

## Discussion of Results

The organic compounds which we have tested for prevention of coprecipitation of traces of thallium with arsenic sulfide (III), possess different chemical properties. Consequently, the fact that we get widely different results during prevention of coprecipitation of thallium with arsenic sulfide, e.g. by Malachite green or gelatin, can be satisfactorily explained, in our opinion, by differences in the surface activity of these materials, and also by the possibility of chemical interaction between some of them and arsenic sulfide (III).

TABLE 3

Prevention of Coprecipitation of Thallium with $As_2S_3$ Using Organic Materials. Rate of Saturation with Hydrogen Sulfide 50-60 Bubbles/Minute; to 100°; Amount of $As_2S_3$ 0.1 g, Tl 14.2 γ; HCl Concentration of 0.3 N; Amount of Organic Materials 50 mg; Formaldehyde 3 ml, Salicylaldehyde 3 ml.

| Test | Organic Material | Thallium coprecipitated | |
|---|---|---|---|
| | | in γ | in % |
| 1 | None added | 14.1 | 99.2 |
| 2 | Malachite green | 0.3 | 2.1 |
| 3 | Brilliant green | 0.27 | 1.9 |
| 4 | Methyl violet | 1.7 | 12.0 |
| 5 | Fuchsine diamond | 1.56 | 11.1 |
| 6 | Neutral red | 0.49 | 3.5 |
| 7 | Methylene blue | 2.4 | 11.2 |
| 8 | Aniline yellow | 8.3 | 58.6 |
| 9 | Rhodamine B | 6.3 | 44.2 |
| 10 | Gelatin | 2.6 | 18.2 |
| 11 | Tannin | 7.6 | 53.3 |
| 12 | Starch | 5.9 | 41.5 |
| 13 | Saponin | 9.7 | 68.1 |
| 14 | Formaldehyde | 12.1 | 85.3 |
| 15 | Salicylaldehyde | 11.6 | 81.7 |

As our results have shown the most efficient suppressors of thallium coprecipitation with $As_2S_3$ are the basic dyes of the triphenylmethane series, and certain azines. These compounds which possess strong surface active properties, are adsorbed on the sulfides and appear to be positively charged sols which interact with the negatively charged sol of $As_2S_3$. Moreover, the subsequent stage of the process may be the formation of surface active compounds. The overall effect of the factors considered, is the reason for the observed sharp decrease in coprecipitation in the presence e.g. of Malachite green, Brilliant green, and Neutral red.

A study of the influence of the protective colloid type of material shows that it prevents coprecipitation of thallium with $As_2S_3$ to a much smaller extent. It is difficult to accept the hypothesis of chemical interaction with sulfides, for this group of materials, while their surface active properties are not clearly expressed. It is of interest to note that gelatin is a much better coprecipitation suppressor than starch.

The rate with which the solution is saturated with hydrogen sulfide, and the temperature of the solution are of great importance for prevention of thallium coprecipitation, as experiment showed. A slow throughput of hydrogen sulfide, just like heating the solution, leads to coarser particles.

It would be of interest to study the effect of the factors considered on a number of other sulfides having basic or acidic characteristics and showing large differences in structure.

In conclusion I wish to thank I. P. Alimarin, Corresponding Member of the USSR Academy of Sciences, for directing this work.

## SUMMARY

1. The effect of certain basic dyes, protective colloids, and aldehydes on prevention of coprecipitation of traces of thallium with arsenic sulfide (III) has been studied.

2. It has been found that lowering the rate of saturation of solution with hydrogen sulfide and raising the temperature, considerably increase the efficiency of the substances enumerated above as coprecipitation suppressors of thallium with arsenic sulfide.

3. It has been shown that basic dyes are the best coprecipitation suppressors. Brilliant green cuts down coprecipitation from 99.2 to 1.9%, Neutral red from 99.2 to 3.5%, and Malachite green from 99.2 to 2.1%.

4. Surface active agents of the hydrophilic colloid type suppress coprecipitation of thallium with arsenic sulfide inappreciably; e.g. saponin suppresses coprecipitation from 99.2 to 68.1%; starch – from 99.2 to 41.5%; tannin – from 99.2 to 53.3% and gelatin from 99.2 to 18.2%.

Received May 14, 1955

## LITERATURE CITED

[1] N. A. Rudnev, J. Anal. Chem, 8, 1, 3 (1953) (T. p.1).*

[2] I. P. Alimarin, N. A. Rudnev, and L. I. Guseva, "Symp. Use of Labeled Atoms in Anal. Chem.", Acad. Sci. Press, Moscow, 1955.

[3] I. L. Teodorovich, V. V. Rakhimova, J. Anal. Chem., 9, 5, 293 (1954) (T. p. 325).*

[4] J. Caldwell, H. Moyer, J. Am. Chem. Soc., 59, 90 (1937).

[5] J. Flagg, J. Am. Chem. Soc. 63, 3150 (1941).

[6] J. Caldwell, H. Moyer, J. Am. Chem. Soc., 57, 2372 (1935).

[7] N. A. Figurovsky and N. N. Ushakova, Factory Labs., 16, 9, 1063 (1950).

* T. p. = C. B. Translation

BLANK
PAGE

# COPRECIPITATION OF THALIUM WITH MERCURY AS THE TETRATHIOCYANATE DIAMINO CHROMITE

N. T. Voskresenskaya

The M. V. Lomonosov Moscow State University, Geochemical Faculty

Serious difficulties crop up during the quantitative determination of microgram amounts of thallium because of the absence of reliable and sensitive enough methods for determining it. This often necessitates preliminary enrichment with thallium, i.e. concentration of the thallium in the test sample.

Among the methods which have been described for its concentration are those based on precipitation of thallium with metallic zinc, extraction of thallium trichloride with ether, and precipitation of thallium with the sulfides of lead and mercury [1]. Alimarin and Ivanov-Emin separated thallium as the slightly soluble iodide [2]. All the same, these methods are not specific enough and are often very cumbersome to carry out.

For separating thallium from other elements, and for its concentration we decided to precipitate thallium as the complex salt—tetrathiocyanate diamino chromite, on the assumption that this reaction is selective enough. Comparatively few cations: $Hg^{2+}$, $Cd^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Bi^{3+}$, $Sn^{2+}$, $Pt^{2+}$, $Ag^{+}$, $Cu^{+}$, $Au^{+}$, $Tl^{+}$ [3] react with ammonium tetrathiocyanate diamino chromite, $NH_4[Cr(CNS)_4(NH_3)_2]$ (Reinecke's Salt). By taking into account the fact that some of these elements are very seldom found with thallium (Pt, Sn, Au, Hg), while interference from others can be prevented by using suitable solvents and complexing agents, this list of elements can be cut down to a minimum (Ag, Cd, and Cu), so that this reaction can be made selective for thallium under the given conditions. Methods based on interaction with Reinecke's salt have been described in the literature for the determination of mercury [4], copper [5], cadmium [6], and thallium [7]. Only the reaction with mercury is highly sensitive and this enabled A. A. Saukov to develop a nephelometric method for determining small amounts of mercury.

The method proposed by Bagbanly for the gravimetric determination of thallium as the reineckate cannot be used for the determination of microgram amounts of this metal, despite the fact that its sensitivity is greater than the method of determining thallium as the iodide or chromate [7], because of the comparatively high solubility of thallium reineckate. Neither Bagbanly nor anybody else as far as we know, has determined the solubility of thallium reineckate. Obviously the problem is complicated by the absence of a highly sensitive reaction for thallium.

The use of radioactive indicators simplifies the problem and permits determination of the thallium content of a saturated solution of thallium reineckate with sufficient accuracy.

We used radioactive thallium-204, which is a $\beta$- and $\gamma$-emitter with a $\beta$-ray energy of 0.765 Mev and is characterized by a half-life period of $2.71 \pm 0.05$ years, for determining the solubility of thallium reineckate.

We had at our disposal a solution of thallium nitrate obtained by dissolving metallic thallium in nitric acid. Radioactive thallium, also as $TlNO_3$ with a known content of thallium, was introduced into this solution.

The Reinecke's salt was prepared from the calculated amounts of chromium chloride $CrCl_3 \cdot 3H_2O$, ammonium thiocyanate, and ammonia. A freshly prepared, saturated solution of the Reinecke's salt was used to prepare thallium reineckate. Thallium reineckate was precipitated from a solution acidified to 0.16 N sulfuric acid, by adding excess of the Reinecke's salt solution. The precipitate thallium reineckate, which was of a rose color, was allowed to stand for 1-2 hours; it was then filtered, washed with water on the filter and transferred to a flask containing 100 ml of distilled water for determination of its solubility.

The flask was placed in a thermostat in which it was kept at $18 \pm 0.1°$ and periodically shaken. Equilibrium is established in 24-30 hours.

After standing, the solution was filtered through a dry filter into a dry beaker. The first portion of filtrate was

rejected, in order to avoid adsorption, while the rest of the filtrate was transferred to a buret. The solution in this buret was then measured out dropwise on to a glass dish 25 mm in diameter and with a rim 1-1.5 mm high placed on a sand bath. After evaporation of a measured amount of the filtrate to dryness, the activity of the dry residue was measured on the dish on a torsion counter.

The specific activity of the original solution of thallium nitrate from which the thallium reineckate was prepared, was determined by measuring the activity of part of the solution, diluted so that a solution with a volume of 50 ml had an activity similar to that of 50 ml of a saturated solution of thallium reineckate.

Results on the solubility determination are given in Table 1. All tests were made in duplicate. The table contains the mean results.

TABLE 1

Solubility of Thallium Reineckate at 18°, Determined Radiometrically

| Number of test | Specific activity of the original solution in impulses/minute/mg | Volume of the saturated solution of thallium reineckate taken for measurements in ml | Activity of the solution taken for measurement in impulses/minute. | Activity of 100 ml of a saturated solution of thallium reineckate in impulses/minute | Solubility of thallium reineckate | |
|---|---|---|---|---|---|---|
| | | | | | $10^{-3}$ mg/ml Tl | $10^{-6}$ mol/liter |
| 1 | 263 | 50 | 27 | 54 | 2.05 | 10.0 |
| 2 | 162 | 45 | 14 | 31 | 1.91 | 9.4 |
| 3 | 162 | 50 | 13 | 26 | 1.60 | 7.8 |
| 4 | 462 | 50 | 39 | 78 | 1.69 | 8.3 |
| 5 | 462 | 40 | 28 | 70 | 1.52 | 7.5 |
| 6 | 300 | 50 | 26 | 52 | 1.73 | 8.5 |
| 7 | 300 | 35 | 20 | 56 | 1.86 | 9.1 |
| | | | | Mean | 1.76 | 8.7 |

If one compares the solubility of thallium reineckate ($8{\cdot}7{\cdot}10^{-6}$ mol/liter) with that of the iodide ($2{\cdot}56{\cdot}10^{-4}$ mol/liter) [8], it is easy to see why the gravimetric method of determining thallium as the reineckate is much better than the gravimetric method using the iodide.

All the same, the solubility of thallium reineckate is still high enough to preclude its use for the determination of microgram amounts of thallium, as is done for mercury [4]. We decided to use this reaction for coprecipitation of microgram amounts of thallium with a suitable carrier. We decided on mercury as the carrier as it has two essential advantages over other elements: 1) mercury reineckate has a very low solubility, 2) mercury can be easily removed subsequently from the precipitate by heating.

In the present article, therefore, we shall consider some of the questions relating to the nature of the coprecipitation of thallium with mercury as the reineckate, and the practical conclusions to be drawn from this study on how to control the given process to get the necessary results. In studying the nature of coprecipitation it is important to establish whether isomorphous substitution or adsorption of the thallium by the precipitate of mercury reineckate occurs. In all our tests we used the radioactive isotope of thallium — $Tl^{204}$ as $TlNO_3$. First of all, the relation between the amount of coprecipitated thallium and the concentration of the coprecipitant - mercury - was studied. These experiments were carried out as follows. Into a weighed 50 ml beaker was introduced 1.5γ of $Tl^{204}$ as $TlNO_3$, having an activity of 2240 impulses /minute, 5 ml of 2 N $H_2SO_4$, 0.2 g $NH_4CNS$, and varying amounts of a 0.001 M solution of $Hg(NO_3)_2$, and the reineckate precipitated by addition of 10 ml of a saturated solution of Reinecke's salt. The precipitate was allowed to stand for 6-8 hours and then filtered. The filtrates, after evaporation, were measured with a β-counter. We reckon that it is methodologically more correct to determine the activity of the filtrates, since the volume of the precipitates obtained varies. Moreover, the accuracy is higher. The amount of coprecipitated thallium was calculated by difference between its activity in the original solution and in the filtrate.

The results obtained are adduced in Table 2.

TABLE 2

| Number of test | Mercury concentration in mg/ml | % Tl precipitated |
|---|---|---|
| 1 | 0.0008 | 58.0 |
| 2 | 0.002 | 67.0 |
| 3 | 0.004 | 74.0 |
| 4 | 0.008 | 91.0 |
| 5 | 0.016 | 94.0 |
| 6 | 0.024 | 98.0 |
| 7 | 0.032 | 98.0 |

TABLE 3

Effect of acidity on thallium coprecipitation

| Number of test | Normality with respect to $H_2SO_4$ | Tl precipitated in % |
|---|---|---|
| 1 | 0.16 | 99.0 |
| 2 | 0.40 | 98.0 |
| 3 | 0.72 | 98.0 |
| 4 | 0.80 | 98.0 |

As these results show, coprecipitation of thallium from solutions in which its concentration is 0.03 γ/ml is satisfactory at mercury concentrations not less than 0.024 mg/ml. We carried out a test in which the thallium was coprecipitated with exactly the same weight of mercury but at a lower concentration (half the previous concentration - 0.012 mg/ml). In this instance, it was found that the amount of coprecipitated thallium decreased to 89-90%. Decreasing the concentration of thallium to a tenth, i.e. to 0.003γ / ml had no effect on the completeness of its coprecipitation.

This can only be explained, in our opinion, on the basis of the nature of the coprecipitation of thallium which we tried to find out about in further work.

By carrying out tests similar to those described above we clarified the effect of acidity on the coprecipitation of thallium. Results are given in Table 3.

The results given in Table 3 show that thallium is coprecipitated from fairly acid solution and that changes in acidity within a wide range have no essential effect on the completeness of its coprecipitation.

In order to clear up the problem of the nature of the coprecipitation of thallium with mercury, a series of experiments was carried out to study the effect on thallium coprecipitation of such factors as temperature, and also the effect of other ions which can affect or do not affect the charge on the surface of the coprecipitant. In addition, precipitation of thallium on precipitates of mercury reineckate formed previously was studied.

The following method was adopted. In one test, to a 25 ml flask was added 5 ml of a 0.001 M solution of $Hg(NO_3)_2$, 2 ml of 2 N $H_2SO_4$, 1.5γ Tl as $TlNO_3$, 0.2 g $NH_4CNS$, 10 ml of a saturated solution of Reinecke's salt, and water added to bring the volume up to 25 ml. The precipitate was allowed to stand at room temperature for 30 hours with periodic shaking.

In another test, the precipitate after separation, was heated on a water bath at 50° for 1 hour and then left for 30 hours at room temperature and shaken during that period.

In a third test, 1 mg of Fe as $FeCl_3$ was added together with the thallium before precipitation as the reineckate.

Experiments designed to study adsorption of thallium on ready-made mercury reineckate were also carried out under varying conditions. In some tests, thallium was introduced into the flask immediately after precipitation of the mercury reineckate, without removal of the mother liquor, while in others the precipitate of mercury reineckate was filtered, washed with water, and then transferred together with the filter to a tared flask into which 2 ml of 2 N $H_2SO_4$ and 1.5 γ of $Tl^{204}$ had been placed beforehand, and the volume made up to 25 ml. In a third test, 0.1 mg of Hg as $Hg(NO_3)_2$ was added to the flask as well as the acid and thallium. In a fourth test the precipitate of mercury reineckate was first saturated with mercury ions. To do this, it was shaken for 1 hour with 5 ml of 0.001 M $Hg(NO_3)_2$ solution in the presence of 2 ml 2N $H_2SO_4$; the precipitate was then filtered, washed with water and transferred to a flask which already contained 1.5γ $Tl^{204}$ and 2 ml of 2N $H_2SO_4$ in a volume of 25 ml.

In addition, coprecipitation and precipitation of thallium were studied on coarse crystalline precipitates of mercury reineckate.

In all tests the contents of the flasks were periodically shaken during the 30 hours. After standing, the precipitate was filtered through dry filters into dry flasks; the first portions of the filtrates were rejected, and after evaporation of an aliquot part of the filtrate (5 ml) on glass dishes, the activity of the dry residue was determined with a torsion counter. The percent amount of coprecipitated and precipitated thallium was determined from the difference between the activity of the original solution and that of the filtrate.

The activity of the original solution, containing 1.5γ $Tl^{204}$ in 25 ml, was determined after a tenfold dilution, by measuring the activity of a portion of the solution evaporated on a glass dish.

The activity of 5 ml of such a solution was shown to be 187 impulses /minute, while the activity of 5 ml of the filtrates from the different test varied from 30-1800 impulses/minute.

The value of the activity was calculated as the arithmetic mean of 10-12 measurements. The results of these tests are given in Table 4 as the arithmetic mean of duplicates.

The results obtained are a satisfactory confirmation of the adsorptive character of the coprecipitation of thallium with mercury as the reineckate.

On the basis of the results given in Table 4 it is possible to draw the following conclusions:

1) Adsorption of thallium by the mercury reineckate precipitate is independent of temperature from 16-50°.

2) Adsorption of thallium is independent of the presence of other cations in solution, which do not form insoluble reineckates and are not adsorbed on the surface of the mercury reineckate.

3) Adsorption of thallium decreases sharply (up to 4%) in the presence of excess mercury ions which are adsorbed on the surface of mercury reineckate to which they communicate a positive charge and appear to act as competitors with thallium. Finally, thallium is practically completely unadsorbed on the surface of mercury reineckate preliminarily given a positive charge by mercury anions.

TABLE 4

| Number of test | Experimental Conditions | % Thallium transferred | |
|---|---|---|---|
| | | Fine crystalline mercury reineckate precipitate | Large crystalline mercury reineckate precipitate |
| 1 | Coprecipitation of Tl and Hg at room temperature | 98 | 85 |
| 2 | Coprecipitation of Tl and Hg on heating the precipitates to 50° for 1 hour | 98 | |
| 3 | Coprecipitation of Tl and Hg in the presence of 1 mg Fe as $FeCl_3$ | 98 | 85 |
| 4 | Precipitation of Tl on a ready-made precipitate of mercury reineckate without removal of the mother liquor (in the presence of excess Reinecke's salt). | 97 | 94 |
| 5 | Precipitation of Tl on a ready-made precipitate of mercury reineckate in the absence of Reinecke's salt | 94 – 96 | 46 |
| 6 | Precipitation of Tl on a ready-made precipitate of mercury reineckate in the presence of $Hg^{2+}$ ions and in the absence of Reinecke's salt | 4.1 | |
| 7 | Precipitation of Tl on a ready-made precipitate of mercury reineckate, charged positively as a result of adsorption of mercury ions | 2.0 | |

4) Adsorption of thallium increases in the presence of $[Cr(CNS)_4(NH_3)_2]^-$ ions which communicate a negative charge to the surface of the adsorbent.

5) Adsorption of thallium varies directly with the size of the surface of the adsorbing surface. This probably explains the fact that adsorption of thallium decreases with decreasing mercury concentration, since, under these conditions, larger crystals of the mercury reineckate are formed.

Thus, the adsorption of thallium follows Hahn's rule:, "In aqueous solution an ion is readily adsorbed on a salt-

forming adsorbent, if the latter has a well developed surface, and if the ion, by uniting with the oppositely charged ion of the lattice, forms a slightly soluble or slightly dissociated compound" [9].

From all that has been said above, the following practical conclusions, which may be used for coprecipitating thallium with mercury reineckate, can be drawn:

1) Coprecipitation of thallium can be carried out in fairly acid solution.

2) Other cations present in solution do not interfere with this coprecipitation as long as they do not form slightly dissociated or insoluble compounds with Reinecke's salt.

3) Coprecipitation must be carried out in the presence of excess precipitant—Reinecke's salt.

4) Coprecipitation must be carried out from cold solutions, having a mercury concentration of not less than 0.024 mg/ml, in order to form a finely dispersed precipitate of mercury reineckate.

On the basis of these conclusions we got good results for the coprecipitation of thallium during the analysis of feldspar to which thallium had been added in amounts of 1·5γ/g and 1·5γ/10 g which correspond to a thallium content in the mineral of $7.5 \cdot 10^{-5}$% and $1.5 \cdot 10^{-5}$%. The amounts of thallium coprecipitated in these cases was 97-98%. Further work on the practical use of this method of coprecipitating thallium continues along the line of developing a method for determination of thallium in minerals, rocks, and ores.

## SUMMARY


1. Using the radioactive isotope $Tl^{204}$, the solubility of the complex salt thallium tetrathiocyanate diamino chromite, which is important in analytical chemical practice, has been determined. At 18° the solubility of this salt is $8.7 \cdot 10^{-6}$ mol/liter.

2. Coprecipitation of thallium with mercury as the reineckate has been suggested for the isolation and concentration of microgram amounts of thallium.

3. Using the radio-isotope $Tl^{204}$, optimal conditions have been established for the quantitative coprecipitation of thallium; these conditions include temperature, acidity, concentration of coprecipitant, and dilution.

4. It has been shown that coprecipitation of thallium with mercury is an adsorptive process.

5. By using this technique it has been found possible to increase the concentration of thallium during analysis of feldspar from $(1.5-7.5) \cdot 10^{-5}$ % to $(1.5-7.5) \cdot 10^{-3}$%, ie. a hundredfold.



Received April 20, 1955


## LITERATURE CITED


[1] E. B. Sandell, "Colorimetric Determination of Traces of Elements" State Chem. Press, 1949.

[2] I. P. Alimarin and B. I. Ivanov-Emin, J. Appl. Chem. 9, 1124 (1936).

[3] I. L. Bagbanly, Bull. Azerbaidzhan Acad. Sci. No. 11, 81 (1946).

[4] A. A. Saukov, Proc. Acad. Sci. 20, 375 (1938).

[5] I. L. Bagbanly, Bull. Azerbaidzhan Acad. Sci. 6, 88 (1947).

[6] Ch. L. Rulfs, E. P. Przybylowicz, C. E. Skinner, Anal. Chem. 26, 408 (1954).

[7] I. L. Bagbanly, Proc. Azerbaidzhan Acad. Sci. 9, 373 (1953).

[8] V. Hildebrand and G. Lendel," A Practical Manual on Inorganic Chemical Analysis" Gen. Sci. Tech. Press, 416 (1937).

[9] O. Hahn, "Applied Radiochemistry", State Chem. Press, 1947, p. 154. (Translation)

BLANK
PAGE

# THE ANALYTICAL CHEMISTRY OF RHENIUM

D. I. Ryabchikov and A. I. Lazarev

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Academy of Sciences, USSR, Moscow

Hitherto, little attention has been given to the analytical chemistry of rhenium. Nevertheless there is a real need for methods for the quantitative determination of rhenium both in natural materials, and in various special alloys to which rhenium has been added.

The $ReO^-_4$ anion forms slightly soluble precipitates with organic bases. Salts are formed with nitron, brucine, 9-amino-acridine, 3, 6-diaminoacridine etc. [1]. Reactions with nitrogen-containing bases are non-specific.

Only nitron is used for its quantitative determination [2]. Tetraphenylarsonium chloride forms a precipitate with perrhenates at a pH of 8-9, which is soluble in chloroform [3]. Triphenylbenzylphosphonium chloride behaves similarly [4]. Sodium diethyldithiocarbamate reacts with rhenium in strongly acid media to form a brown precipitate which is soluble in organic solvents [5].

A considerably greater number of reactions are known for septivalent rhenium. A solution of potassium ferrocyanide forms a brown precipitate with rhenium; the reaction occurs in an acid medium in the presence of $SnCl_2$ [6,7].

Dimethylglyoxime reacts with rhenium salts in the presence of acid and $SnCl_2$ to give a reddish color, while on heating, the solution fluoresces. $\alpha$-Furildioxime [8], and $\alpha$-benzyldioxime [9], react with rhenium salts in the same way as dimethylglyoxime.

The behavior of $\alpha$-dioximes with rhenium salts in the presence of acid and reducing agents has been studied in detail by Peshkova and Gromova [10]; they studied the conditions of formation of rhenium complexes with methyldioxime, dimethylglyoxime, $\alpha$-furildioxime, and o-cyclohexanedioxime. Rhenium, according to these authors, is quadrivalent in the compounds formed.

Interaction of rhenium compounds ( < VIII) with $\alpha$-dioximes in acid media permit one to conclude that the atomic group

is characteristic for ions of rhenium in lower valency states, probably quadrivalent.

Its complex compounds with thiocyanates are widely used for colorimetric determination of rhenium. The reaction takes place in acid media in the presence of a reducing agent [11].

The compounds of rhenium (IV) react with tetrone to form a precipitate [12].

Kuznetsov [13], points out that the chromophoric combinations of atoms $Re^{<+7}-S-$; $Re^{<+7}-N<$, are characteristic for rhenium. This is confirmed by the reactions which we describe below.

Poluektov [14], has developed a sensitive method of determining rhenium, which is based on the catalytic action of the latter on the reduction of sodium tellurate with $SnCl_2$.

The reactions enumerated above practically exhaust the list of articles published at home and abroad on the analytical chemistry of rhenium.

On the basis of the theory of the chromophoric action of elements, we studied the behavior of rhenium toward organic reagents containing various combinations of atoms —hydroxylamine, urea, thiourea, thiosemicarbazide, diphenylthiourea, sodium ethyl xanthogenate, red streptocide, Methyl violet, zircon, rhodamine, 2-thiohydantoin, haemotoxylin, $\beta$-naphthaquinoline, rivanol and diethyldithiophosphoric acid. In all cases, tests were carried out in 25 ml flasks into which had been introduced 0.20 mg of rhenium as sodium perrhenate, acid, and test reagent. Rhenium

exhibits different valency states in its compounds.

Colored products were obtained with thiourea and thiosemicarbazide in the presence of hydrochloric acid, $SnCl_2$ or $TiCl_3$.

At the same time it was established that urea does not ensure the development of a color when rhenium has a valency less than VII, under similar conditions. Potassium ethylxanthogenate, in the presence of $SnCl_2$, forms a white precipitate soluble in organic solvents.

Addition of a 1% solution of diethyldithiocarbamate in water to a hydrochloric acid solution of perrhenate, in the presence of $SnCl_2$, leads to the formation of a precipitate which is extractable with diethyl ether. Rhenium is not present in the aqueous phase in this instance. Here, apparently, the formation of a combination of reactive atoms of diethyldithiocarbamate with rhenium in low valency states guarantees the necessary reaction. A 0.5% solution of diphenylthiourea [16] in alcohol forms a weakly colored precipitate in the presence of $SnCl_2$. The low solubility of the compound formed can be explained apparently by the presence of phenyl groups in the molecule.

Reactions of Rhenium with Thiourea and Thiosemicarbazide.

The reaction between rhenium and thiourea was studied on an FEK-M photoelectro-colorimeter. The solution of rhenium compound was acidified with hydrochloric acid (1.19) to which was added a 5% aqueous solution of thiourea and a 20% solution of $SnCl_2$ in hydrochloric acid. The total volume amounted to 25 ml.

It was found that the color intensity of the complex compound formed depends on the acidity.

TABLE 1

The effect of acidity on the color intensity of rhenium-thiourea complex compound

| Acid concentration in g-equivalents/liter | Light absorption $\log \frac{I_0}{I_1}$ |
|---|---|
| 0.5 | 0.340 |
| 1.0 | 0.520 |
| 2.0 | 0.690 |
| 3.0 | 0.705 |
| 4.2 | 0.718 |
| 5.0 | 0.710 |
| 6.0 | 0.478 |
| 8.0 | 0.362 |

TABLE 2

Relation between the color of the rhenium-thiourea complex and thiourea concentration

| Thiourea concentration | Light absorption $\log \frac{I_0}{I_1}$ |
|---|---|
| 0.00 | 0.000 |
| 0.006 | 0.340 |
| 0.013 | 0.505 |
| 0.026 | 0.610 |
| 0.040 | 0.642 |
| 0.053 | 0.674 |
| 0.080 | 0.669 |
| 0.106 | 0.675 |

Best results were obtained at an acidity of not less than 3-5 N hydrochloric acid (taking into account the acidity of the $SnCl_2$ solution).

The color increases with increasing concentration of thiourea up to $5 \cdot 10^{-2}$ mole/liter. Further addition of thiourea to the solution has practically no effect on the color.

It is clear from Fig. 1 that the color of the solution develops slowly; 40-50 minutes are necessary to get comparable results.

Heating of the solution favors a more rapid development of color. Nevertheless, on heating the solution above 75°, the solution browns, presumably as the result of decomposition of thiourea to give rhenium sulfides. The color is completely developed in 5-7 minutes at 65-75°.

Maximum sensitivity is obtained on the photoelectric colorimeter when a No. 3 blue filter is used.

Light absorption of solutions of the rhenium-thiourea complex does not follow the Lambert-Beer law (Fig. 2) either at low or high concentrations.

On the basis of these tests it is possible to suggest a colorimetric method for determining rhenium by means of thiourea. A solution containing the rhenium salt is acidified with 5 ml HCl (1.19). To this is added 5 ml of a 5% aqueous thiourea solution and 1 ml of $SnCl_2$. The solution obtained is made up with distilled water to 25 ml in a standard flask; it is then shaken and heated for 5-10 minutes on a water bath at 65-75°. The cooled solution is colorimetrically measured using a No. 3 blue filter. By means of this method it is possible to determine down to 10-15 μ g of rhenium

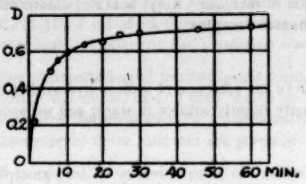



Fig. 1. Effect of time on the development of the rhenium color (0.600 mg).

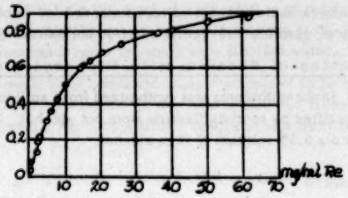



Fig. 2. Relation between light absorption of the rhenium-thiourea complex and rhenium concentration.

in a volume of 25 ml. The rhenium-thiourea complex is insoluble in organic solvents, so that the sensitivity of the method cannot be increased. The accuracy of the method amounts to ± 5% relative. Comparative results on the determination of rhenium are adduced in Table 3. Better agreement between results is obtained if the solution is allowed to stand for 50-60 minutes without heating it.

TABLE 3

Accuracy of the colorimetric method of determining rhenium with thiourea

| Rhenium taken in mg | Rhenium found in mg | Error in mg |
|---|---|---|
| 0.020 | 0.019 | −0.001 |
| 0.037 | 0.037 | 0.000 |
| 0.048 | 0.049 | +0.001 |
| 0.056 | 0.056 | 0.000 |
| 0.056 | 0.058 | +0.002 |
| 0.093 | 0.096 | +0.003 |
| 0.112 | 0.117 | +0.005 |
| 0.166 | 0.171 | +0.005 |
| 0.180 | 0.188 | +0.008 |
| 0.250 | 0.238 | −0.012 |

The accuracy of the thiourea method for rhenium is comparable to that of the thiocyanate method [15]. The method was checked on mixtures of metallic tungsten and rhenium (Table 4). Tungsten was separated from rhenium chromatographically.

Oxidizing agents present in large amounts $NO_3^-$ $ClO_3^-$ $Cr_2O_7^{2-}$ $MnO_4^-$ $BrO_3^-$ destroy the color.

Fluorides, citrates, tartrates, and oxalates do not interfere with the reaction at concentrations up to 1 g-equivalent/liter.

TABLE 4

Results of determinations of rhenium in alloys by means of the thiourea and thiocyanate methods

| Taken in mg | | Rhenium found in mg | |
|---|---|---|---|
| W | Re | by the thiocyanate method | by the thiourea method |
| 87.0 | 3.8 | 3.63 | 3.70 |
| 72.6 | 4.8 | 4.81; 4.74 | 4.72; 4.68 |
| 52.4 | 4.2 | 4.15; 4.20 | 4.24; 4.16 |

Low results were obtained in the presence of ions of mercury (II), cadmium (II), and bismuth (III), since these ions form stable complexes with thiourea. Solutions containing up to 0.5 mg molybdenum (VI), and tungsten (VI) give high results. Tartaric acid masks the action of the elements indicated to some extent.

Interference from antimony (III) is easily masked by addition of fluoride ions. Tellurium, selenium, and arsenic (III) separate out in the free state and interfere with the reaction. It should be noted that formation of the rhenium-thiourea complex occurs in the presence of titanium (III) also.

Substitution of hydrochloric acid by sulfuric acid leads to the appearance of a brownish color instead of the yellow-green obtained in hydrochloric acid medium.

The rhenium-thiosemicarbazide complex is orange in color. It is formed on pouring together solutions of the

rhenium compounds, thiosemicarbazide, hydrochloric acid, and $SnCl_2$. The color develops very slowly and, therefore, thiosemicarbazide cannot be recommended for colorimetric determination of rhenium. Amyl acetate, chloroform, benzene, gasoline and diethyl ether do not extract the rhenium-semicarbazide complex.

## Reaction of Rhenium with Diphenylthiourea.

Diphenylthiourea was synthesized from aniline and carbon disulfide in the presence of sodium hydroxide [16]. It was purified by recrystallization from hot alcohol. Diphenylthiourea is only slightly soluble in water and we accordingly used a 0.5% solution of it in alcohol.

TABLE 5

Results of the separation of rhenium from pure solutions with diphenylthiourea

| Rhenium taken in mg | Rhenium found in mg |
|---|---|
| 0.003 | 0.002 |
| 0.007 | 0.006 |
| 0.013 | 0.011 |
| 0.027 | 0.027 |
| 0.042 | 0.040 |
| 0.084 | 0.086 |
| 0.170 | 0.162 |
| 0.340 | 0.327 |

Perrhenates form a weakly colored precipitate which is only slightly soluble in water, with diphenylthiourea in the presence of $SnCl_2$ or $TiCl_3$ as reducing agents, and hydrochloric acid or sulfuric acid.

We examined the possibility of isolating rhenium from its pure solutions by means of this slightly soluble precipitate. To a solution of rhenic acid was added 5 ml HCl (1.19), 1-2 ml of a 0.5% solution of diphenylthiourea in alcohol, and 1 ml of a 20% solution of $SnCl_2$. The solution was made up to a volume of 25 ml with distilled water. After mixing and then standing for one hour, the turbid solution was filtered through a No. 3 sintered glass crucible. Heating does not speed up formation of a precipitate. The precipitate was washed on the filter with 25 ml of 2 N hydrochloric acid + 0.5 ml of a solution of diphenylthiourea. The washed precipitate was dissolved in a solution of sodium hydroxide or 5% ammonia, hydrogen peroxide being added dropwise.

Rhenium was determined colorimetrically in the alkaline filtrate with potassium thiocyanate.

The results which are given in Table 5 show that the sensitivity of the method amounts to 0.15 μg/ml of rhenium.

Molybdenum (VI) does not form a precipitate under these conditions. The complexing agents —fluorides, oxalates, tartrates, and citrates—do not interfere with the formation of the rhenium-diphenylthiourea complex.

The rhenium-diphenylthiourea complex is soluble in organic solvents: diethyl ether, chloroform, carbon tetrachloride, and isoamyl alcohol. We did not carry out quantitative tests on the extraction of the rhenium-diphenylthiourea, which is only slightly soluble in water, with the aid of these solvents.

## Composition of Rhenium Complex Compounds.

The complex compound formed between rhenium and diphenylthiourea was separated from solution, dried over sulfuric acid and analyzed for its rhenium and sulfur content. Sulfur was determined by the Eshk method; rhenium-colorimetrically in the presence of thiocyanate and thiourea. The following analytical results were obtained:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Aliquot taken | 15.0 mg, | Re | found | 15.5%, | Re | calculated | 15.98% |
| " | " 10.4 mg | Re | " | 15.8 | Re | " | 15.98% |
| " | " 19.8 mg | S | " | 10.5 | S | " | 10.98% |
| " | " 61.6 mg | S | " | 10.8 | S | " | 10.98% |

On the basis of these results the following formula can be suggested for this compound.

$$\left[ReO_2\left(S=C\begin{matrix}NH-C_6H_5\\NH-C_6H_5\end{matrix}\right)_4\right]Cl$$

The composition of the rhenium-thiourea complex was investigated by Ostromyslensky's method of studying the light absorption of solutions of it [17]. A solution of rhenic acid was prepared by dissolving an aliquot of metallic rhenium in 10 ml of HCl (1:1), to which hydrogen peroxide was added dropwise. Solution was carried out in a 50 ml flask fitted with an air condenser. After the metal had dissolved, the solution was boiled to destroy hydrogen peroxide and to remove chlorine. The cooled solution was diluted with distilled water to 1 liter. The rhenium concentration was checked by precipitating it with nitron acetate [18]. The reducing agent was prepared before the test by dissolving 0.2 - 0.3 g of tin foil in HCl (1:19) in a $CO_2$ atmosphere. A 5% thiourea solution was obtained by dissolving thiourea

in thoroughly boiled distilled water.

In order to determine the valency of rhenium in its complex with thiourea, the solutions prepared were introduced into a 25 ml flask in a definite order: the solution of rhenic acid, 5 ml HCl (1.19), 4 ml of a 5% solution of rhenic acid, 5 ml HCl (1.19), 4 ml of 5% thiourea solution. After careful mixing the solution was heated for 10 minutes at 65-70° on a water bath. Finally the $SnCl_2$ solution was added and the solution made up to the mark with distilled water.

The concentration of the $SnCl_2$ and rhenic acid solution was equal; their combined volume amounted to 15 ml. The solution was mixed up and then heated on a water bath for a further 15 minutes. It was then cooled and submitted for colorimetric determination on a photoelectro-colorimeter fitted with a No. 3 blue filter. Results of this study of the light absorption of these solutions are given in Table 6.

It is evident from the results given in Table 6 that maximum optical density is observed for a ratio of $HReO_4$ : $SnCl_2$ of 1:1. This permits the interaction of rhenic acid with $SnCl_2$ to be represented by the equation:

$$ReO^-_4 + Sn^{2+} + 4H^+ = ReO^+_2 + Sn^{4+} + 2H_2O.$$

On the basis of this reaction it is possible to conclude that rhenium is in a quinquevalent state in the rhenium-thiourea complex. Sometimes, on pouring the solutions together, a lilac color is first obtained, which subsequently, changes over into a greenish-yellow color. This lilac color is probably the result of the formation of a compound of sexivalent rhenium (VI).

TABLE 6

Light absorption of solutions of stannous chloride and rhenium

| Taken in ml | | Ratio | Light absorption | Observations |
|---|---|---|---|---|
| $HReO_4$ | $SnCl_2$ | Re:Sn | $\log \frac{I_0}{I_1}$ | |
| 2.5 | 12.5 | 0.2 | 0.100 | |
| 3.5 | 11.5 | 0.3 | 0.196 | |
| 4.5 | 10.5 | 0.4 | 0.315 | |
| 5.0 | 10.0 | 0.5 | 0.364 | Cuvette width −10 mm |
| 6.0 | 9.0 | 0.7 | 0.436 | $C_{Re} = C_{Sn} = 1.65 \cdot 10^{-3}$ mole/liter |
| 7.5 | 7.5 | 1 | 0.522 | |
| 9.0 | 6.0 | 1.5 | 0.426 | |
| 10.0 | 5.0 | 2 | 0.358 | |
| 11.2 | 3.8 | 3 | 0.340 | |
| 2.5 | 12.5 | 0.2 | 0.186 | |
| 3.5 | 11.5 | 0.3 | 0.390 | |
| 5.0 | 10.0 | 0.5 | 0.540 | Cuvette width −50 mm |
| 6.0 | 9.0 | 0.7 | 0.560 | $C_{Re} = C_{Sn} = 1.35 \cdot 10^{-3}$ mole/liter |
| 7.5 | 7.5 | 1 | 0.610 | |
| 9.0 | 6.0 | 1.5 | 0.442 | |
| 12.5 | 2.5 | 5 | 0.223 | |

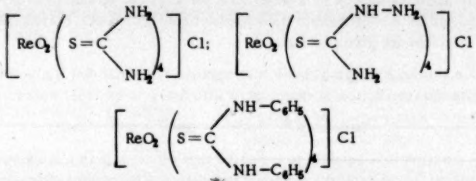
Of no little importance is the sign of the charge of the colored moiety in determining the composition of complex compounds; this can easily be determined by means of ion-exchange resins.

A solution of the rhenium-thiourea complex was prepared by mixing solutions of 0.300 g of rhenium, 10 ml HCl (1.19), 8 ml of 5% thiourea solution and 2 ml of 20% $SnCl_2$. After an hour, a solution prepared in this way was passed through a column 10 mm in diameter containing 10 g of the anion-exchange resins TM and MMG-1 in the OH- form at a rate of 3 ml/minute. The filtrate obtained was of the same color as the original solution. It follows therefore, that the colored part of the complex is not absorbed by the active groups of the ion-exchange resin. On passing a similar solution through a column filled with cation-exchange resins sulfo-coal K and SBS in the H-form, on the other hand, complete absorption of the colored part of the complex occurred, so that the filtrate was colorless. Tests with ion exchange resins give a convincing proof of the cationic nature of the colored part of the rhenium thiourea complex.

The colored part of the complex formed between rhenium and thiosemicarbazide is also a cation. This compound behaves similarly to the rhenium-thiourea complex with ion-exchange resins.

The behavior of the complex compounds of rhenium with semi-carbazide and thiourea, respectively, toward ion-exchange resins, the fact that the conditions under which the reactions are carried out are identical. The similarity between the atomic groupings in thiourea, thiosemicarbazide, and diphenylthiourea, permit one to consider that the three complexes they form with rhenium are of the same type.

On the basis of this study the following formulas can be ascribed to the compounds of rhenium with these reagents:



## Composition of the Rhenium Thiocyanate Complex

The best known method of determining rhenium colorimetrically is the thiocyanate method. The composition and structure of the rhenium-thiocyanate complex formed during this reaction have not yet been accurately established.

In the literature, the probable formulas $ReO(SCN)_4$ [18], or $ReO(SCN)_3$ [19], are usually ascribed to this complex. One of us [20], suggested that the probable composition of the rhenium-thiocyanate complex can be expressed by the formula $K[ReO(SCN)_4]$.

In order to ascertain the true composition of the complex we used ion-exchange chromatography, and studied the light absorption of solutions of the complex.

The solutions, and the order in which they were added together, were the same as used for the preparation of the rhenium-thiourea complex. An aqueous solution of potassium thiocyanate was used instead of thiourea solution. The reducing agent, $SnCl_2$, was added after the solution had been cooled.

Colorimetric measurements were carried out on an FEK-M photoelectro-colorimeter using a blue filter.

TABLE 7

Light absorption of solutions of rhenium + thiocyanate

| Taken in ml | | Ratio | Light absorption | Observations |
|---|---|---|---|---|
| $HReO_4$ | KCNS | KCNS:$HReO_4$ | $\log \frac{I_0}{I_1}$ | |
| 1.0 | 9.0 | 9 | 0.159 | Cuvette width – 50 mm |
| 2.0 | 8.0 | 4 | 0.214 | $C_{Re} = C_{SCN^-} = 0.000284$ mole/liter |
| 2.5 | 7.5 | 3 | 0.211 | |
| 5.0 | 5.0 | 1 | 0.190 | |
| 6.0 | 4.0 | 0.48 | 0.132 | |
| 1.0 | 9.0 | 9 | 0.166 | Cuvette width – 50 mm |
| 2.0 | 8.0 | 4 | 0.262 | $C_{Re} = C_{SCN^-} = 0.000400$ mole/liter |
| 2.5 | 7.5 | 3 | 0.250 | |
| 3.0 | 7.0 | 2.3 | 0.196 | |
| 5.0 | 5.0 | 1 | 0.106 | |
| 1.0 | 9.0 | 9 | 0.242 | Cuvette width – 50 mm |
| 1.5 | 8.5 | 5.1 | 0.314 | $C_{Re} = C_{SCN^-} = 0.000500$ mole/liter |
| 2.0 | 8.0 | 4 | 0.326 | |
| 2.5 | 7.5 | 3 | 0.298 | |
| 3.0 | 7.0 | 2.3 | 0.240 | |
| 4.0 | 6.0 | 0.7 | 0.188 | |

It follows from the results given in Table 7 that the maximum optical density is obtained for a ratio of KCNS : $HReO_4$ of 4 : 1. This means that the complex can be represented by the formulas

$ReO(SCN)_4$, $K[ReO(SCN)_4]$ and $K_3[ReO_2(SCN)_4]$.

The behavior of the rhenium-thiocyanate complex on ion-exchange resins was also studied, and this can be a deciding factor in selecting the correct formula. A colored solution obtained by pouring together 15 ml HCl (1.19), 2 ml of 25% KCNS solution, 0.30 mg perrhenate, and 2 ml of 20% $SnCl_2$ in a volume of 50 ml, and standing for 15 minutes, was passed through a cation exchange resin. The filtrate collected after passage through sulfo coal K in the H-form was colored the same as the original solution. The filtrate collected after passing a similar solution through an anion-exchange resin in the $OH^-$ form was colorless, while the top part of the anion-exchange column had a reddish color. Washing the column with 0.5 N HCl did not remove the color. On passing a solution of 1 N sodium hydroxide through the anion-exchange column, the color was washed off the column into the filtrate, which thereby acquired the color of the original solution.

The behavior of the rhenium thiocyanate complex toward ion-exchange resins confirms the anionic character of the colored part of the complex.

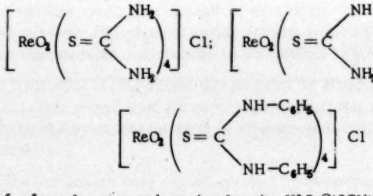
One can conclude from these tests that the rhenium-thiocyante complex can be represented by the formulas $K[ReO(SCN)_4]$ and $K_3[ReO_2(SCN)_4]$ in which, apparently rhenium is quinquevalent, while the colored part of the complex is a complex anion. On the basis of the results obtained, one can assume that the rhenium-thiocyanate complex is formed according to the reaction:

$$ReO_4^- + Sn^{2+} + 4SCN^- + 6H^+ = [ReO(SCN)_4]^- + Sn^{4+} + 3H_2O.$$

## SUMMARY

1. The behavior of rhenium with different organic reagents has been studied.

2. Complex compounds of rhenium with thiourea, thiosemicarbazide, and diphenylthiourea have been examined; their composition can be expressed by the formulas:



3. The correctness of a formula suggested previously, viz. $K[ReO(SCN)_4]$ for the rhenium-thiocyanate complex has been demonstrated.

4. It has been shown that it is possible to use ion-exchange resins for studying complex compounds.

5. A new colorimetric method, in which thiourea is used as reagent, has been suggested for rhenium.

Received November 22, 1954

## LITERATURE CITED

[1] I. Drutse, "Rhenium" Foreign Lit. Press (1951).

[2] W. Geilmann, A. Voigt, Z. anorg. Chem. 193, 311 (1930).

[3] S. Tribilat, Annal. Chem. Appl. 3, 113, (1949).

[4] S. Tribilat, Anal. chim. Acta 5, 115 (1951).

[5] Yu. A. Chernikhov and V. M. Dobkina, Factory Labs. 10, 1143 (1949).

[6] A. Tougarinoff, C. 1934, II, 1499.

[7] S. Tribilat, Annal. Chem. Appl. 4, 289 (1949).

[8] S. A. Fisher, V. W. Meloche, Anal. Chem. 7, 1100 (1952).

[9] S. Tribilat, Chem. Abstr. 3339 (1947).

[10] V. M. Peshkova and M. I. Gromova, Bull. Moscow University , 10, 85 (1952).

[11] W. Geilmann, F. W. Wrigge, F. Weibke Z. anorg. Chem. 208, 217 (1932).

[12] S. Tribilat, Anal. chim. Acta 2, 138 (1952).

[13] V. I. Kuznetsov, Prog. Chem. 2, 173 (1952).

[14] N. S. Poluektov, J. Appl. Chem. 12, 2312 (1936).

[15] E. B. Sandell "Colorimetric Determination of Traces of Metals" State Chem. Press, 1949.

[16] L. M. Kulberg, "Syntheses of Organic Reagents", State Chem. Press, 1947, p. 102.

[17] I. I. Ostromyslensky, Ber. 44, 268 (1911).

[18] G. F. Druce, Rec. trav. chim. Pays-Bas 54, 334 (1935).

[19] V. I. Bibikova, Rare Metals, 6, 24, (1935).

[20] D. I. Ryabchikov, J. Anal. Chem. 1, 34 (1952).(T. p. 35) *

* T. p. = C. B. Translation pagination.

# INVESTIGATION OF COMPLEX COMPOUNDS OF THE URANYL ION WHICH ARE OF IMPORTANCE IN ANALYTICAL CHEMISTRY. I

N. P. Komar and Z. A. Tretyak

The A. M. Gorky Kharkov State University

In previous articles [1,2], it has been shown that determination of the composition of complexes, of the constants of the respective equilibriums, and of molar extinction coefficients is complicated if the metal ion is subjected to hydrolysis and forms complexes with components of the buffer mixture, while the addenda are anions of weak acids used as reagents. In the same articles general methods of work and special apparatus for use in systems of this type were suggested.

As the first test object for trying out these new methods of investigation we chose the $UO_2^{2+}$ ion since, according to published results [3, 4], it gives only one hydrolysis product—the $UO_2OH^+$ ion, so that the system is not too complicated as a result of hydrolysis. It was precisely with the study of such a relatively simple system that we started to check new spectrophotometric methods.

Uranyl nitrate, the original reagent was crystallized successively, first from ether and then from water. The last crystallization from aqueous solution, on slight evaporation, gave characteristic, large crystals of the hexahydrate. After a preliminary drying in air these crystals were ground and left in air till they were of constant weight. Special analyses showed that the salt thus prepared corresponded to the formula $UO_2(NO_3)_2 \cdot 6H_2O$.

The original 0.200 M solution of uranyl nitrate was prepared by dissolving an aliquot; its concentration was checked gravimetrically. All other uranyl solutions were prepared from this stock solution by dilution, the volumes of standard flasks and pipets being chosen so that the error in all operations connected with the preparation of the various solutions did not exceed 0.10%.

All measurements of optical density were carried out on a spectrophotometer using a UM-2 monochromator, the wave scale of which was checked with 37 different lines in the spectra of mercury, neodymium, and zinc. A special check, using three sectors, the value of whose transmissions of 0.663, 0.457 and 0.3305, confirmed by measurements on a microphotometer, showed that there was a strict linear relationship between the divisions on the galvanometer scale and the light flow falling on the photo-elements of the photometric set-up of the apparatus. Since the cells used in the UM-2 were not suitable, we had to use cells from an FEK set-up; special brass arresting devices were used to fix these other cells on the stage. This simple gadget proved very convenient in use, since completely reproducible results could be obtained by manual adjustment. An approximate check on the thickness of the layer of each cell reduced to measurements of the optical density of a bromophenol blue solution. The results obtained showed that the figures given with the cells were correct; these values were therefore used for all further measurements. In all determinations discussed in this paper, the widths of the entrance and exit slits were adjusted to give a band width for the light beam from the spectrum pole of 3.0 mμ. Corresponding values of the width of the slit were obtained for varying wavelengths from a calibration curve calculated from data on prism dispersion supplied with the monochromator.

A Chechik set-up was used for supplying the lamp [5], since the stabilizer supplied with the UM-2 did not provide good enough voltage stabilization.

Measurements of optical density were carried out in the following order:

1) the opening of the diaphragm of the entrance slit was adjusted to 10-15 mm;

2) the wave drum was rotated to a position corresponding, according to the calibration data, to the selected wave length;

3) the widths of the entrance and exit slits were adjusted to give a band width of 3 mμ;

4) the galvanometer reading $I_0^{II}$ for unweakened light was noted, i.e. when the cell is not in position;

5) the galvanometer reading I after placing the cell filled with "solvent" on the stage was noted;

6) the galvanometer reading $I_0^{I}$ for cell filled with "solution" was taken.

Readings were repeated 3-5 times; mean values were used for calculating the optical density. The optical density of the solvent was determined from the values of $I_0^{II}$ and I; the value obtained was then subtracted from the optical density of the solution calculated for the same cell from the values of $I_0^{II}$ and I.

The optical density of the solution determined in this way determines the true adsorption of the colored material found in the system.

Measurements of hydrogen ion concentration were made electrometrically on a set-up which included a Rapp's potentiometer, a saturated calomel electrode as reference electrode, and a quinhydrone electrode. The possibility of measuring pH in solutions containing $UO_2^{2+}$ ions by means of a quinhydrone electrode has been demonstrated [4] by means of parallel determinations using a glass electrode.

The results of all measurements were treated statistically at a working level of $\alpha = 0.95$ [6, 7].

First of all, we drew an absorption curve for aqueous solutions of uranyl nitrate whose concentration was varied from 0.010 to 0.500 mole/liter. It is clear from the graph (Fig. 1, curve a) that these solutions absorb in the violet, the maximum absorption being observed at 420 mμ.

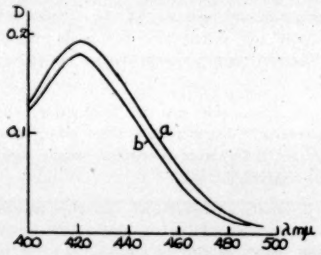


Fig. 1.

Comparison of the optical density-wave length (D, λ) curves obtained for an aqueous solution of uranyl nitrate, and a solution of the same concentration, but containing 0.05 mole of free $HNO_3$/liter, shows (Fig. 1, curbe b), that on acidification, the character of the curve (D, λ), does not change but a decrease in the absorptive capacity of the system is observed. Similar changes in optical density were obtained on acidifying the uranyl nitrate solution with the same amount of hydrochloric acid.

Since such a weakening of the absorptive capacity may be connected with the formation of uranyl chloro- and nitrate complexes, the existence of which cannot be doubted [8, 9], it was necessary to carry out special tests to clarify this side of the question. Mixtures were therefore prepared which contained 20 ml of a 0.0200 M solution of uranyl nitrate and 20 ml of a 0.100 solution of potassium or sodium chloride and potassium or sodium nitrate. In each of these mixtures the initial concentration of the nitrate or chloride ions were the same as in tests with the corresponding acids; nevertheless, the graph of D, λ now practically coincided with the graph for 0.0100 M uranyl nitrate not containing constant additions.

The results obtained showed that, for the initial concentrations of $NO_3^-$ and $Cl^-$ we studied, no appreciable formation of nitrate or chloro complexes occur, so that in this connection one must assume that the absorption changes, primarily, as a result of changes in pH of the solution, which result from hydrolysis and the formation of uranyl hydroxy complexes; whose absorption bands lie practically in the same part of the visible spectrum, but differ with respect to the value of the molar extinction coefficients.

According to published results [4], in the pH range 0.1 to 1.55 the $UO_2^{2+}$ ion is dominant, at higher pH's $UO_2OH^+$ ions are formed, while ions of even greater complexity can be formed. A spectrophotometric study of this equilibriated system should start with a study of the molar extinction coefficients ($\epsilon$) of the components existing in the most acid solutions. Optical densities were measured of solutions in which the initial concentration of the $UO_2^{2+}$ ion ($c_{UO_2^{2+}}$) was kept constant, while the initial hydrogen ion concentration ($c_{H^+}$) was altered within fairly wide limits. Results of measurements carried out for four series of solutions, differing in their values of $c_{UO_2^{2+}}$, showed that up to a pH of 3, the optical density increases gradually, while at a pH of $\geqslant 3$ it has a practically constant value. These values were used for calculating the molar extinction coefficients of the $UO_2^{2+}$ ions, since there are indications that at a pH < 2.5, only this ion exists. Values of the optical density obtained in one of the series of tests are given in Table 1, while the values of $\epsilon_{UO_2^{2+}}$, calculated by means of the formula $D/lc_{UO_2^{2+}}$, are given in Table 2.

TABLE 1

Results of the determination of the optical density (D) of uranyl nitrate solutions for various initial concentrations of the $H^+$ ions. $c_{UO_2^{2+}} = 4.004 \cdot 10^{-3}$ mole/liter. Layer thickness $l = 5.010$ cm

| Number of test | $C_{H^+}$ in mole/liter | $D_{420}$ | $D_{430}$ |
|---|---|---|---|
| 1 | – | 0.1748 | 0.1503 |
| 2 | $1.00 - 10^{-4}$ | 0.1709 | 0.1449 |
| 3 | $2.00 - 10^{-4}$ | 0.1657 | 0.1411 |
| 4 | $3.00 - 10^{-4}$ | 0.1600 | 0 1386 |
| 5 | $4.00 - 10^{-4}$ | 0.1565 | 0.1325 |
| 6 | $5.00 - 10^{-4}$ | 0.1515 | 0.1225 |
| 7 | $1.00 - 10^{-3}$ | 0.1428 | 0.1184 |
| 8 | $5.00 - 10^{-3}$ | 0.1428 | 0.1165 |
| 9 | $9.00 - 10^{-3}$ | 0.1428 | 0.1145 |

TABLE 2

Results of determinations of molar extinction coefficients of the $UO_2^{2+}$ ions ($\epsilon_{UO_2^{2+}}$) at various wave lengths ($\lambda$)

| $\lambda$ in m$\mu$ | Number of measurements | $\bar{\epsilon}_{UO_2^{2+}}$ | $s^2$ | Accuracy $\delta_{0.95}$ | Relative error in % |
|---|---|---|---|---|---|
| 420 | 27 | 7.30 | 0.25 | $\pm$0.20 | 2.7 |
| 430 | 24 | 6.09 | 0.16 | 0.17 | 2.8 |
| 440 | 24 | 3.40 | 0.12 | 0.15 | 4.4 |

$\epsilon_{UO_2OH^+}$ was determined by means of a special formula, while the values of D obtained for pH >3 were used, since, according to one hypothesis [4], $UO_2^{2+}$ and $UO_2OH^+$ coexist under these conditions. It was assumed that hydrolysis follows the equation:

$$UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+.$$

Let us assume that $c_{UO_2^{2+}} = c$, then for any $[H^+] = h_i$, measured electrometrically, $[UO_2OH^+] = x_i$ and $[UO_2^{2+}] = c - x_i$ and according to the law of mass action

$$\frac{h_i x_i}{c - x_i} = K \qquad (1)$$

If for a given wave length $\epsilon_{UO_2OH^+} = \epsilon_x$, while $\epsilon_{OH_2^{2+}} = \epsilon$ determined previously, then in the i'th experiment

$$D_i = (c - x_i)\,\epsilon l + x_i \epsilon_x l, \qquad (2)$$

while for the same $c_{UO_2^{2+}} = c$, but with pH < 2, the optical density

$$d = c\,\epsilon l \qquad (3)$$

and subtracting (3) from (2) we find that

$$x_i = \frac{\Delta_i}{l(\epsilon_x - \epsilon)}, \qquad (4)$$

where $\Delta_i = D_i - d$. Substituting the values of $x_i$ from equation (4) in (1), we get, for the i' th experiment the equation

$$h_i \Delta_i = K[lc(\epsilon_x - \epsilon) - \Delta_i], \qquad (5)$$

containing two unknown constants: K and $\epsilon_x$. By combining equation (5) with a similar equation for the K' th experiment, we get the equation for calculation:

$$\epsilon_x = \epsilon + \frac{\Delta_i \Delta_k (h_i - h_k)}{lc(h_i \Delta_i - h_k \Delta_k)} \qquad (6)$$

Results of calculations of $\epsilon_{UO_2OH^+}$ according to formula (6) for one of the four series of measurements are given

in Table 3, while Table 4 contains results of a statistical treatment of all the values of $\epsilon_{UO_2OH^+}$ which were obtained. The values of $\bar{\epsilon}$ and $s^2$ for all four series of measurements were combined, since it was shown that the differences between them were random. By using the values of $\epsilon_{UO_2^{2+}}$ and $\epsilon_{UO_2OH^+}$ at 420 mμ, we were able to calculate the values of $x_i$ by means of formula (4), and then calculated the hydrolysis constant of the uranyl ion. An example of such a calculation for one series of measurements is given in Table 5, while the statistical treatment of all the results of the 17 measurements are given in Table 6.

TABLE 3

Results of determinations of $\epsilon_{UO_2OH^+}$ at 420 mμ. $c_{UO_2^{2+}} = 4.004 \cdot 10^{-3}$ mole/liter; d = 0.1428; l = 5.010 cm

| $D_{420}$ | $\Delta_i$ | $\Delta_k$ | $h_i$ in mole/liter | $h_k$ in mole/liter | $\epsilon_{UO_2OH^+}$ |
|---|---|---|---|---|---|
| 0.1709 | 0.0281 | | $1.00\ 10^{-4}$ | | |
| 0.1657 | | 0.0229 | | $2.00 \cdot 10^{-4}$ | 9.11 |
| 0.1600 | | 0.0172 | | $3.00 \cdot 10^{-4}$ | 9.41 |
| 0.1565 | | 0.0137 | | $4.00 \cdot 10^{-4}$ | 9.46 |
| | 0.0229 | | $2.00\ 10^{-4}$ | | |
| | | 0.0172 | | $3.00 \cdot 10^{-4}$ | 10.85 |
| | | 0.0137 | | $4.00 \cdot 10^{-4}$ | 10.78 |
| | 0.0172 | | $3.00\ 10^{-4}$ | | |
| | | 0.0137 | | $4.00 \cdot 10^{-4}$ | 10.64 |

TABLE 4

Values of $\epsilon_{UO_2OH^+}$ at 420 mμ

| λ in mμ | n | $\bar{\epsilon}$ | $s^2$ | $\delta_{0.95}$ | Error in % |
|---|---|---|---|---|---|
| 420 | 26 | 10.9 | 1.4 | 1.6 | 14.6 |

TABLE 5

Results of the determination of the hydrolysis constant of the $UO_2^{2+}$ ion with $c_{UO_2^{2+}} = 4.004 \cdot 11^{-3}$ mole/liter; d = 0.1428, l = 5.010 cm

| Number of experiment | $D_{420}$ | $[UO_2OH^+]$ $x_i \cdot 10^3$ mole/liter | $[UO_2^{2+}]$ $(c - x_i)\,10^3$ mole/liter | $[H^+]$ $h \cdot 10^4$ mole/liter | $K \cdot 10^5$ | $\bar{K} \cdot 10^5$ |
|---|---|---|---|---|---|---|
| 1 | 0.1709 | 1.56 | 2.45 | 1.00 | 6.37 | |
| 2 | 0.1657 | 1.27 | 2.73 | 2.00 | 9.29 | 8.3 |
| 3 | 0.1600 | 0.95 | 3.06 | 3.00 | 9.31 | |
| 4 | 0.1565 | 0.76 | 3.24 | 4.00 | 9.37 | |

TABLE 6

Results of the determination of the hydrolysis constant of the uranyl ion, obtained by statistical treatment of the results of four series of experiments

| n | $\bar{K}$ | $s^2$ | $\delta_{0.95}$ |
|---|---|---|---|
| 17 | $6.4 \cdot 10^{-5}$ | $8.9 \cdot 10^{-6}$ | $0.5 \cdot 10^{-5}$ |

The values which we got for the hydrolysis constant differ to only a small extent from the value of $8.1 \cdot 10^{-5}$ found polarographically [3]. At the same time, the hydrolysis constant $K_H$, calculated by means of the formula $K_H = K_{H_2O} / K_{UO_2OH^+}$, was found to be $5 \cdot 10^{-6}$, i.e., a tenth of the other. In calculating this value it was assumed that for equilibrium

$$UO_2^{2+} + OH^- \rightleftharpoons UO_2OH^+, \quad K = 2 \cdot 10^9 \text{ [4]}.$$

For a decisive explanation of the possibility of forming acido-complexes of the uranyl ion with chloride and nitrate ions noted in the literature [8, 9], and in order to explain their effect on the optical density of solutions of uranyl salts, it was necessary to study the relation between the optical density of solutions with a constant concentration of $UO_2^{2+}$ ions, but with an increasing concentration of $Cl^-$ or $NO_3^-$ ions (saturation curve).

Table 7 contains results for one series of tests on a study of (D, x) diagrams. In this case, 0.01 M solutions of uranyl nitrate and potassium chloride, at a pH of 3 was used, while optical density was measured for a layer of thickness 5.01 cm. As a result in Table 7 show, the value of the optical density for certain wave-lengths (420 and 430 m $\mu$) decrease regularly with decreasing initial concentration of uranyl ions. It is possible to suggest therefore, in this connection that at the $Cl^-$ ion concentrations at which we were working, according to Ostromyslensky's method [10], appreciable amounts of uranyl chloro-complexes are not formed. To check this hypothesis the values found for the optical density were used for calculating the molar extinction coefficients $\epsilon_{420}$ and $\epsilon_{430}$ which are also given in Table 7. The usual statistical treatment of the results [7], gave the following values: $\bar{\epsilon}_{420} = 7.52$; $s^2_{420} = 0.14$; $n = 8$; $\bar{\epsilon}_{430} = 6.08$; $s^2_{430} = 0.012$; $n = 8$.

TABLE 7

Results of a study of the optical properties of a system containing varying initial amounts of 0.01 M solutions of $UO_2(NO_3)_2$ and KCl. The total volume in all cases was 40 ml. The thickness of the absorbing layer was 5.01 cm.

| Number of experiment | Solutions taken | | $c_{UO_2^{2+}}$ in mole/liter · $10^3$ | Found $D_{420}$ | Calculated $\epsilon_{420}$ | Found $D_{430}$ | Calculated $\epsilon_{430}$ |
|---|---|---|---|---|---|---|---|
| | $UO_2^{2+}$ in ml | $Cl^-$ in ml | | | | | |
| 1 | 40.00 | – | 10.00 | 0.3687 | 7.36 | 0.3065 | 6.12 |
| 2 | 32.00 | 8.00 | 8.00 | 0.2900 | 7.24 | 0.2380 | 5.94 |
| 3 | 30.00 | 10.00 | 7.50 | 0.2690 | 7.16 | 0.2256 | 6.00 |
| 4 | 26.60 | 13.40 | 6.67 | 0.2435 | 7.29 | 0.2018 | 6.04 |
| 5 | 20.00 | 20.00 | 5.00 | 0.1815 | 7.25 | 0.1500 | 5.99 |
| 6 | 13.40 | 26.60 | 3.33 | 0.1272 | 7.63 | 0.1045 | 6.26 |
| 7 | 10.00 | 30.00 | 2.50 | 0.1030 | 8.22 | 0.0780 | 6.23 |
| 8 | 8.00 | 32.00 | 2.00 | 0.0805 | 8.03 | 0.0603 | 6.02 |
| | | | | Total | 60.18 | | 48.60 |
| | | | | Mean | 7.52 | | 6.08 |

At the same time, as the results in Table 2 show, the results obtained previously were: $\bar{\epsilon}_{420} = 7.30$; $s^2_{420} = 0.25$; $n = 27$ and $\bar{\epsilon}_{430} = 6.09$; $s^2 = 0.16$; $n = 24$.

A comparison of mean values and dispersions by the methods of mathematical statistics [11], showed that the deviations between them are random. Thus, it is clear, that for a small excess of $Cl^-$ ions, no formation of uranyl chloride complexes is observed.

The values of $\epsilon$ and $s^2$ obtained were used for getting more accurate values of these quantities. As a result, we got the following values $\alpha = 0.95$: $\epsilon_{420} = 7.4 \pm 0.2$ and $s^2 = 0.30$ at $n = 35$; $\epsilon_{430} = 6.1 \pm 0.1$ and $s^2 = 0.12$ at $n = 30$. Exactly similar results were obtained with potassium nitrate solutions.

As a further check on the possibility of forming chloro- and nitrate uranyl complexes, measurements were made of the optical density of mixtures containing a constant concentration of $UO_2^{2+}$ and increasing concentrations of $Cl^-$ or $NO_3^-$ ions. These experiments showed that the optical density of solutions containing a constant initial concentration of uranyl ions remains constant even for a ten-fold excess of the chloride or nitrate ions. Only on increasing the $NO_3^-$ or $Cl^-$ concentration further is a regular increase in optical density detected. Since this change could be ascribed to complex formation, and to a simple increase in concentration of $UO_2OH^+$ ions as a result of an increase in hydrolysis with a consequent increase in ionic strength of the solution, it was necessary to carry out some more tests to check up on this point.

The results of one of the series, which are given in the first three columns of Table 8, illustrate fairly clearly the nature of the change in optical density with changes in the initial concentration of potassium chloride and the value of $\mu$. Since the value of $D_{420}$ changes to exactly the same extent on substituting potassium chloride by the nitrate, this would seem to indicate that it is an ionic strength effect.

According to the law of mass action the equilibrium $UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$ corresponds to the equation

$$\frac{[UO_2OH^+]}{[UO_2^{2+}]} = \frac{K}{[H^+]} \cdot \frac{f_{(2)}}{f^2_{(1)}},$$

TABLE 8

Changes in optical density for solutions containing $4.00 \cdot 10^{-3}$ M of uranyl ion and $4.00 \cdot 10^{-3}$ M hydrochloric acid with increasing concentration of potassium chloride. The optical density was measured ($D_{420}$) at 420 mμ, the thickness of the

| $c_{KCl}$ in mole/liter | $\mu$ | $D_{420}$ | $[UO_2^{2+}]$ in mole/liter $\cdot 10^3$ | $[UO_2OH^+]$ in mole/liter $\cdot 10_3$ | Found $\log \frac{[UO_2OH^+]}{[UO_2^{2+}]}$ | $\frac{\sqrt{\mu}}{1+\sqrt{\mu}}$ | Calculated $\log \frac{[UO_2OH^+]}{[UO_2^{2+}]}$ |
|---|---|---|---|---|---|---|---|
| $3.20 \cdot 10^{-2}$ | 0.048 | 0.1426 | 4.00 | 0.00 | – | 0.1797 | – |
| $9.60 \cdot 10^{-2}$ | 0.112 | 0.1508 | 3.75 | 0.25 | −1.177 | 0.2507 | −1.11 |
| 0.176 | 0.192 | 0.1590 | 3.296 | 0.704 | −0.670 | 0.3048 | −0.79 |
| 0.338 | 0.354 | 0.1650 | 2.963 | 1.037 | −0.456 | 0.3730 | −0.40 |
| 0.496 | 0.512 | 0.1761 | 2.348 | 1.652 | −0.153 | 0.4171 | −0.14 |
| 0.638 | 0.654 | 0.1848 | 1.866 | 2.134 | 0.058 | 0.4471 | 0.04 |

where $f_{(2)}$ -is the activity coefficient of the doubly charged ion, while $f_{(1)}$ -is the singly charged ion. Using the value of the activity coefficients, in accordance with the Debye-Huckel equation for more concentrated solutions [12], we find that

$$\log \frac{[UO_2OH^+]}{[UO_2^{2+}]} = \log \frac{K}{h} = \frac{2A\sqrt{\mu}}{1+\sqrt{\mu}},$$

where A is the Debye-Huckel constant. It is obvious that the changes found for the optical density can be related to the effect of ionic strength only if the relation between $\log([UO_2OH^+]/[UO_2^{2+}])$ and $\sqrt{\mu}/(1+\sqrt{\mu})$ is reasonably well expressed by the equation for a straight line within these coordinates.

Results of the respective calculations are given in the remaining columns of Table 8. The respective values of $[UO_2^{2+}]$ and $[UO_2OH^+]$ are calculated by means of the equations

$$D_i = 5.01\,(7.3\,[UO_2^{2+}]_i + 10.9\,[UO_2OH^+]_i)$$

and

$$[UO_2^{2+}]_i + [UO_2OH^+]_i = 4 \cdot 10^{-3},$$

where i is the number of the respective experiment, 5.01 the thickness of the absorbing layer in centimeters, $\epsilon_{UO_2^{2+}} = 7.3$ and $\epsilon_{UO_2OH^+} = 10.9$. Finally the values of $\log([UO_2OH^+]/[UO_2^{2+}])$ adduced in the last column were calculated by means of the empirical equation of a straight line

$$\log \frac{[UO_2OH^+]}{[UO_2^{2+}]} = -2.589 + 5.882\,\frac{\sqrt{\mu}}{1+\sqrt{\mu}},$$

calculated from values of $\log([UO_2OH^+]/[UO_2^{2+}])$ and $\sqrt{\mu}/(1+\sqrt{\mu})$, which are given in the sixth and seventh columns of Table 8.

A comparison of the results obtained and the calculated values, and also the graph on Fig. 2, show that in the given instance a linear relation holds very closely.

Both these results and similar results, obtained for systems containing increasing concentrations of potassium nitrate, permit one to state that even for a 150-fold excess of $Cl^-$ or $NO_3^-$ ions, no ions of chloro- and nitrate-uranyl complexes exist at all or are formed in such negligible amounts as would require the most sensitive methods for their detection. At the same time, it has been found that the changes in optical density which have been observed, may be explained by electrostatic interaction, at least within the experimental errors of our experiments.

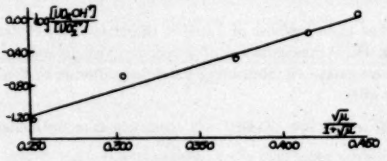



Fig. 2.

## SUMMARY

1. It has been confirmed at at a pH which prohibits the formation of a precipitate of uranyl hydroxide, only $UO_2^{2+}$ and $UO_2OH^+$ ions exist in aqueous solutions of uranyl salts.

2. The molar extinction coefficients of $UO_2^{2+}$ and $UO_2OH^+$ ions have been determined.

3. It has been established that the hydrolysis constant of the uranyl ion according to the equation $UO_2^{2+} + H_2O \rightleftharpoons UO_2OH^+ + H^+$ is given by

$$K = (6.4 \pm 0.5) \cdot 10^{-5},$$

at a confidence level of 0.95, from which it follows that the dissociation constant of the $UO_2OH^+$ ion

$$K_{UO_2OH^+} = 1.6 \cdot 10^{-10}.$$

4. It has been shown that for a 150-fold excess of $Cl^-$ or $NO_3^-$ ions, no appreciable amount of chloro- or nitrate uranyl complexes, the existence of which has hitherto been generally accepted, could be detected.


Received July 14, 1943

## LITERATURE CITED


[1] N. P. Komar, Trans. Inst. Chem. Kharkov State University 12, 53 (1954).

[2] N. P. Komar, Trans. Inst. Chem. Kharkov State University, 12, 61 (1954).

[3] W. E. Harris, I. M. Kolthoff, J. Am. Chem. Soc. 69, 446 (1947).

[4] S. Ahrland, Acta Chemica Scandinavica 3, 374 (1949).

[5] N. O. Chechik, Factory Labs. No. 8, 971 (1947).

[6] E. G. Grachev, J. Anal. Chem. 7, 48 (1952) (T. p. 51). *

[7] N. P. Komar, J. Anal. Chem. 7, 325 (1952) (T. p. 361). *

[8] G. Remi, A Textbook of Inorganic Chemistry, Vol. II, Gen. Sci. Tech. Press, Chem.Theoret., Leningrad, 1935, p. 103.

[9] B. V. Nekrasov, "A Course of General Chemistry" State Chem. Press, 1952, Moscow-Leningrad p. 594.

[10] I. I. Ostromyslensky, Ber. 44, 268 (1911).

[11] V. I. Romanovsky, "Application of Mathematical Statistics in Experimental Work", State Tech. Press, 1947, Moscow-Leningrad, pp. 88 and 89.

[12] S. Glasstone, "Introduction to Electrochemistry", Foreign Lit. Press, Moscow, 1951, p. 196.


* T. p. = C. B. Translationpagination.

BLANK
PAGE

# AMPEROMETRIC STUDY OF THE PRECIPITATION REACTIONS OF SILVER FERROCYANIDE

## II. INVESTIGATION OF THE OXIDATION REACTION OF SILVER FERROCYANIDE.

G. A. Kleibs

Kuibyshev Aviation Institute

A considerable amount of published work has been devoted to insoluble heavy metal ferrocyanides. A considerable part of this work consists of descriptions of individual, empirically developed methods for the quantitative determination of these metals. Work devoted to the study of the processes which occur during formation of these precipitates, and to the nature of these precipitates is relatively small. Of these one must single out the work carried out by I. V. Tananaev and his co-workers [1], who made a physico-chemical study of the formation of some insoluble ferrocyanides.

One of the most important factors which affects the composition of the ferrocyanides formed is the nature and concentration of the alkali metals which are introduced into the reaction mixture at an early stage and are gradually introduced with the ferrocyanide ions.

In a previous article [2] we showed, using a study of the precipitation reaction of copper ferrocyanide as an example, that amperometry is a convenient method for studying the influence of the nature and high concentrations of the alkaline metals on this process.

In the work described in this article we used an amperometric method for studying the effect of sodium and potassium ions on the precipitation of silver ferrocyanide. A study of the precipitation of silver ferrocyanide is of interest in that the ionic radius of silver differs relatively very little from the ionic radius of these alkali metals.

### Experimental Procedure and Original Materials

For this work, a "Geologorazvedka" polarograph with a galvanometer, whose sensitivity of $5.8 \cdot 10^{-9}$ A could be varied by means of an Ayrton shunt, was used.

Since a dropping mercury cathode could not be used for titrating silver ions, a rotating micro-platinum electrode was used as the indicator electrode, the number of revolutions of which remained constant during titration. A saturated calomel electrode was used as the reference electrode.

Contact between catholyte and anolyte was made through a beaker containing potassium chloride using an electrolyte switch filled with a saturated solution of potassium nitrate in agar-agar. 0.1 M silver nitrate was prepared from chemically pure reagent. The concentration of the solution was determined gravimetrically by precipitating it as silver chloride. 0.1 M potassium ferrocyanide was prepared from chemically pure reagent and its concentration determined as described previously [2].

The silver nitrate and potassium ferrocyanide solutions were kept in dark flasks. All other silver nitrate and potassium ferrocyanide solutions used in the course of the work were prepared by dilution of these stock 0.1 M solutions. The indifferent salts of the alkali metals were of analytical quality and were all recrystallized and dried.

0.03–0.05% gelatin was added to the titrant solution as well as the alkali solutions. Such a method was suggested by Kolthoff [3], to prevent the possibility of a reduction at the cathode, of silver from the colloidal particles of silver ferrocyanide formed. Dissolved oxygen was not removed, since the voltage at which we were operating corresponds to the beginning of the reduction wave of oxygen on the cathode.

Titration was carried out at an applied voltage of −0.05 V. Selection of this value was determined by the following considerations; the normal potential of silver is considerably more positive than that of the saturated calomel electrode. According to published results, the solubility of normal silver ferrocyanide is $2.2 \cdot 10^{-9}$ mole/liter [4]. Using this value for the solubility, and the value given for the normal potential of silver, it is easy to calculate that the potential of silver at the end point will still be more positive than the potential of the saturated calomel electrode.

In order to make sure that titration is carried out in the potential range corresponding to the diffusion current of

silver ions, we carried out titration at the applied potential indicated above. Making the potential more negative would necessitate expelling oxygen from the solution. Readings were made on the galvanometer 1-2 minutes after addition of each portion of reagent.

## Experimental Results and Discussion of Results

Precipitation of silver ions by the ferrocyanides of the alkali metals has been studied by several authors [5-7].

Results of this work have shown that when silver salts react with potassium ferrocyanide, formation of both the normal salt $Ag_4[Fe(CN)_6]$ and the double ferrocyanide $KAg_3[Fe(CN)_6]$ is possible.

X-ray studies of silver ferrocyanide by Weiser and co-workers [8], gave two diffraction photographs according to whether the precipitate was formed with excess or insufficient potassium ferrocyanide.

The author reckons that if the existence of two diffraction photographs is not determined by various crystalline modifications of the same compound or its various hydrates, then the one which is obtained in the presence of insufficient potassium ferrocyanide is the normal form, while the other—the double salt—is the one formed when excess potassium ferrocyanide is used.

We planned our experiments so as to try and explain what effect sodium and potassium ions have on the formation of silver ferrocyanide.

Table 1 contains the results of measurements, obtained by direct titration of silver nitrate solution with potassium ferrocyanide in the presence of potassium and sodium nitrates.

Fig. 1 illustrates four of the direct titration curves obtained.

The results which we obtained during a rapid titration of silver ions with potassium ferrocyanide, show that in the presence of sodium ions, the final end point is constant and corresponds to formation of the normal salt (Experiments 1-9, Table 1).

Attention must be drawn to the fact that normal silver ferrocyanide was obtained in these tests independent of what concentrations of silver nitrate and potassium ferrocyanide were used. Moreover, when potassium ferrocyanide was used as reagent, potassium ions were introduced simultaneously with ferrocyanide ions into the solution being titrated, and the concentration of these potassium ions, at a certain stage in the titration, should be enough to ensure formation of the double ferrocyanide from the ions. Nevertheless, as the results given in Table 1 show, it is the normal and not the double salt that is formed. The following conclusions can be drawn from these results:

TABLE 1

Titration of silver nitrate with potassium ferrocyanide in solutions of sodium and potassium nitrate. The volume of $AgNO_3$ solution was 100 ml in all cases.

| Number of experiment | $AgNO_3$ concentration in mole/liter | Concentration of indifferent salt in mole/liter | | $K_4[Fe(CN)_6]$ concentration in mole/liter | Volume of $K_4[Fe(CN)_6]$ solution used | Volume that should be used to form $Ag_4[Fe(CN)_6]$ | Volume that should be used to form $KAg_3[Fe(CN)_6]$ |
|---|---|---|---|---|---|---|---|
| | | $NaNO_3$ | $KNO_3$ | | | | |
| 1 | 0.0002 | 0.1 | – | 0.01 | 0.5 | 0.5 | 0.66 |
| 2 | 0.0002 | 1.0 | – | 0.01 | 0.5 | 0.5 | 0.66 |
| 3 | 0.0002 | 2.0 | – | 0.01 | 0.5 | 0.5 | 0.66 |
| 4 | 0.001 | 0.1 | – | 0.01 | 2.5 | 2.5 | 3.33 |
| 5 | 0.001 | 1.0 | – | 0.01 | 2.5 | 2.5 | 3.33 |
| 6 | 0.001 | 2.0 | – | 0.01 | 2.55 | 2.5 | 3.33 |
| 7 | 0.01 | 0.1 | – | 0.1 | 2.5 | 2.5 | 3.33 |
| 8 | 0.01 | 1.0 | – | 0.1 | 2.55 | 2.5 | 3.33 |
| 9 | 0.01 | 2.0 | – | 0.1 | 2.53 | 2.5 | 3.33 |
| 10 | 0.0002 | – | 0.1 | 0.01 | 0.5 | 0.5 | 0.66 |
| 11 | 0.0002 | – | 1.0 | 0.01 | 0.5 | 0.5 | 0.66 |
| 12 | 0.0002 | – | 2.0 | 0.01 | 0.5 | 0.5 | 0.66 |
| 13 | 0.001 | – | 0.1 | 0.01 | 2.5 | 2.5 | 3.33 |
| 14 | 0.001 | – | 1.0 | 0.01 | 3.1 | 2.5 | 3.33 |
| 15 | 0.001 | – | 2.0 | 0.01 | 3.35 | 2.5 | 3.33 |
| 16 | 0.01 | – | 0.1 | 0.1 | 3.1 | 2.5 | 3.33 |
| 17 | 0.01 | – | 1.0 | 0.1 | 3.50 | 2.5 | 3.33 |
| 18 | 0.01 | – | 2.0 | 0.1 | 3.55 | 2.5 | 3.33 |

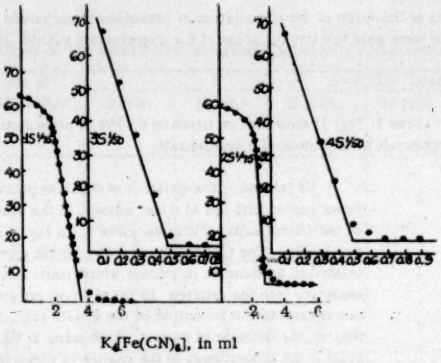



Fig. 1. Titration of 100 ml of 0.01 M $AgNO_3$ with 0.1 M $K_4[Fe(CN)_6]$ in 1 M $KNO_3$(1); in 1 M $NaNO_3$ (2); and of 100 ml 0.0002 M $AgNO_3$ with 0.01 M $K_4[Fe(CN)_6]$ in 1 M $KNO_3$ (3); in 1 M $NaNO_3$ (4).

1. The double ferrocyanide which is obtained under the given conditions is not the result of a direct interaction of silver, potassium and ferrocyanide ions in solution. Its formation is preceded by the formation of the normal salt.

2. Substitution of the silver which enters into the composition of the ferrocyanide by sodium is difficult, and even at a concentration of 2 mole/liter of the latter, it has no effect on the composition of the precipitate.

Our first conclusion agrees with that of Britton and Dodd [7]. These authors, on carrying out a conductometric titration of 0.02 M silver nitrate with 0.1 M potassium ferrocyanide to a constant value for the electrical conductivity, obtained one break on the curve corresponding to formation of the double salt $KAg_3[Fe(CN)_6]$, while a rapid potentiometric titration gave a final end point corresponding to the formation of the normal salt. They concluded that the double salt is formed after the normal salt under these conditions.

The second fact can be explained on the basis that for equal valency of the silver and sodium ions, the ionic radius of sodium is somewhat smaller than that of silver, while cationic exchange takes place the easier, the smaller the ionic radius of the cation coming out of the solid phase, and the greater the ionic radius of the cation replacing it.

Analysis of the results obtained on titrating silver nitrate with potassium ferrocyanide in the presence of potassium nitrate (Table 1, Experiments Nos. 10-18), shows that:

1. Formation of the double salt of silver and potassium ferrocyanide is not easy, since the end point in experiments where 0.0002 M silver nitrate is titrated with 0.01 M potassium ferrocyanide, even in a 2 M solution of potassium nitrate, corresponds to formation of the normal salt. It is absolutely clear that under these conditions there are enough potassium ions in solution to form a double salt.

2. With increasing concentration of the silver nitrate being titrated, the final end point from the addition of potassium salts, is displaced toward formation of the double salt, while equal concentrations of potassium salts displace the final end point to a greater extent, the higher the concentration of the silver solution. Thus, on titrating 0.001 M silver solution with 0.1 M potassium nitrate, the final end point corresponds to the formation of the normal salt. Titration under the same conditions, but of a 0.01 M silver nitrate solution, gives a final end point which lies at values intermediate between points corresponding to the formation of the normal and double salts (Experiments Nos. 13 and 16, Table 1).

These experimental facts lead us to think that the formation of silver ferrocyanide starts with the formation of the normal salt in potassium nitrate as well as in sodium nitrate solutions. This reaction is ionic and is a rapid one; the second stage then follows—interaction of the solid phase with potassium ferrocyanide:

$$3Ag_4[Fe(CN)_6] + K_4[Fe(CN)_6] = 4KAg_3[Fe(CN)_6].$$

Since the reaction is heterogeneous, it depends on the time and the value of the contact surface between the phases on which the interaction takes place has a considerable effect on the reaction velocity.

In some experiments the volume of potassium ferrocyanide exceeds the volume corresponding to the formation of a double salt (Experiments Nos. 17 and 18, Table 1). Apparently, the double salt formed is capable of absorbing some more potassium ferrocyanide on its surface.

Apart from direct titration of silver ions with ferrocyanide ions, since we wished to follow the formation of silver ferrocyanide under conditions such that the concentration of the ferrocyanide ions exceeds the concentration of the silver ions, we carried out a number of back titrations, in which we precipitated the potassium ferrocyanide with silver nitrate.

Since the concentration of potassium ions formed as the result of the dissociation of potassium ferrocyanide in solution is enough to destroy the migration current, we were able to carry out some of the experiments without adding indifferent salts of the alkali metals.

The results obtained are given in Table 2.

The results given in Table 2 (Experiment No. 1, curve 1, Fig. 2) show that on titrating 0.0002 M potassium ferrocyanide with 0.01 M silver nitrate, the end point corresponds to formation of a normal salt.

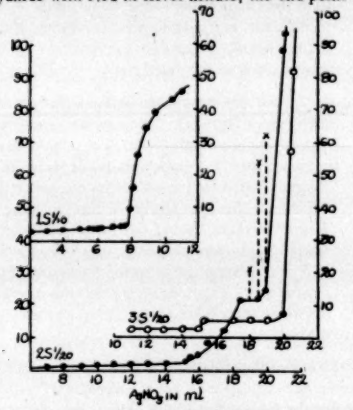



Fig. 2. Titration of 100 ml of 0.0002 M solution of $K_4[Fe(CN)_6]$ with 0.01 M $AgNO_3$ (1); 100 ml of 0.005 M $K_4[Fe(CN)_6]$ with 0.1 M $AgNO_3$ (2); 100 ml of 0.005 M $K_4[Fe(CN)_6]$ with 0.1 M $AgNO_3$ (3); (plotted on the basis of the final value of the current, Table 3).

Of interest is the titration of 0.005 M potassium ferrocyanide with 0.1 M silver nitrate, in the absence of indifferent salts. Titration curve 2, on Fig. 2 has two breaks. The first break, as shown on the curve, is related to an increase in current which starts after introducing into the solution 15 ml of silver nitrate; this corresponds to the formation of the double salt. Nevertheless, the increase in current which starts at this point is not proportional to the change in concentration of silver ions added to the solution, and at a certain stage of the titration, there is even observed a rapid fall in current, the initial growth of which is the result of adding a new lot of reagent (on the curve these maximum values of the current are denoted by crosses). This phenomenon, which indicates that transformations occur in the reaction mixture which are related to the removal of silver ions from solution, is observed up to the point where the added volume of silver nitrate corresponds to formation of the normal salt. After this point the current increases in proportion to the increased concentration of silver ions in solution.

If one takes into consideration the results of back titration, Fig. 1, the first break on the curve can be interpreted as follows: the double salt is formed in the presence in solution of a definite excess of potassium and ferrocyanide ions even during back titration.

TABLE 2

Titration of potassium ferrocyanide solutions with silver nitrate solutions in the absence and in the presence of potassium nitrate. Volume of $K_4[Fe(CN)_6]$ was 100 ml in all cases.

| Number of test | $K_4[Fe(CN)_6]$ concentration in mole/liter | $KNO_3$ concentration in mole/liter | $AgNO_3$ concentration in mole/liter | Volume of $AgNO_3$ used in ml | Amount that should be used for formation of $Ag_4[Fe(CN)_6]$ | Amount that should be used for formation of $KAg_3[Fe(CN)_6]$ | Observations |
|---|---|---|---|---|---|---|---|
| 1 | 0.0002 | – | 0.01 | 7.95 | 8 | 6 | |
| 2 | 0.005 | – | 0.1 | 15;20 | 20 | 15 | 2 breaks obtained on the curve |
| 3 | 0.0002 | 0.002 | 0.01 | 7.3 | 8 | 6 | |
| 4 | 0.0002 | 0.02 | 0.01 | 6.0 | 8 | 6 | |
| 5 | 0.005 | 1.0 | 0.1 | 15 | 20 | 15 | |

The subsequent path taken by the curve and the second break which corresponds to formation of the normal salt show that on adding excess silver ions to the solution, transformation of the double salt into the normal salt begins; the rate of this transformation increases with increasing concentration of silver ions in solution.

Table 3 contains results of titration taken over a period of time.

TABLE 3

Titration of 100 ml of 0.005 M $K_4[Fe(CN)_6]$ with 0.1 M silver nitrate

| Volume of $AgNO_3$ added | S = 1/20. Readings on the galvanometer at | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 1 min. | 5 min. | 10 min. | 15 min. | 20 min. | 25 min. | 30 min. | Corrected values for dilution |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 |
| 6 | 2 | 2 | 3 | 3 | 3 | 3 | 3 | 3.18 |
| 11 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3.33 |
| 12 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3.36 |
| 13 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3.39 |
| 14 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3.42 |
| 15 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3.45 |
| 15.2 | 4 | 5 | 5 | 5 | 5 | 5 | 5 | 5.76 |
| 17.0 | 8 | 8 | 6 | 5 | 5 | — | 5 | 5.85 |
| 18.0 | 10 | 9 | 9 | 6 | 5 | 5 | 5 | 5.90 |
| 19.0 | 10 | 9 | 8 | 6 | 5 | 5 | 5 | 5.95 |
| 20 | 16 | 7 | 6 | 6 | 6 | 6 | 6 | 7.2 |
| 20.5 | — | 38 | 48 | 48 | 48 | 48 | 48 | 57.84 |
| 20.8 | — | 68 | 68 | 68 | 68 | 68 | 68 | 82.14 |

After addition of each aliquot of reagent, the current was read after 1 minute and then every 5 minutes till a constant value was obtained. The latter values were corrected for dilution. Titration curve 3 (Fig. 2) was drawn using the final corrected values. There are also two breaks on this curve corresponding to the formation of the double and normal salt: the height of the first break is, however, very small. Its presence can be explained by the fact that, at this stage of the titration, as a result of the insignificant excess of silver ions in solution, the exchange between these and the potassium ions of the precipitate is very slow.

Experiments 3, 4, and 5 in Table 2 show that addition of $KNO_3$ shifts the titration end point and leads to formation of the double salt.

Thus, the results of back titration of potassium ferrocyanide with silver nitrate show that the cationic exchange between potassium and silver ions in the test process is reversible and its direction depends to a considerable extent on the concentration of the reactants.

## SUMMARY

1. The reaction between silver nitrate and potassium ferrocyanide in solutions of potassium and sodium nitrate has been studied amperometrically.

2. It has been established that this reaction can occur with formation of the normal silver ferrocyanide $Ag_4[Fe(CN)_6]$ and the double salt $KAg_3[Fe(CN)_6]$.

3. Formation of a solid phase starts with precipitation of normal silver ferrocyanide. Formation of a double salt is the result of a secondary process, based on the interaction of precipitated normal salt with ferrocyanide and potassium ions found in solution.

4. During back titration, in the absence of indifferent salts of potassium, excess silver ions in solution can lead to the transformation of the double salt to the normal salt.

5. Addition of sodium nitrate to the solution, even in amounts of 2 mole/liter, does not change the composition of the precipitated normal silver ferrocyanide.

Received February 8, 1954

## LITERATURE CITED

[1] I. V. Tananaev and M. I. Levina, J. Anal. Chem. 1, 224 (1946). 3, 31 (1948); Factory Labs, 15, 887 (1949); I. V. Tananaev and A. S. Kozlov, J. Anal. Chem. 6, 149 (1951); I. V. Tananaev and E. S. Dzhaparidze, J. Gen. Chem. 21, 1000 (1951). (T. p. 1097) *.

[2] N. G. Chovnyk and G. A. Kleibs, J. Anal. Chem. 3, 303 (1948).

[3] H. A. Laitenen, I. M. Kolthoff, Phys. Chem. 45, 1079 (1941).

[4] I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis", Vol. I, (1950).

[5] W. D. Treadwell, D. Chervet, Helv. Chim. Acta 6, 550 (1923).

[6] W. Meyer, Z. anal. Chem. 74, 108 (1928).

[7] H. Britton, E. Dodd, J. Chem. Soc. 1543 (1933).

[8] H. Weiser, W. Milligan, I. Bates, J. Phys. Chem. 42, 945 (1938).

* T. p. = C. B. Translation pagination.

# THE USE OF FILMS OF SILICO-ORGANIC COMPOUNDS IN ULTRA-MICRO-ANALYSIS

I. P. Alimarin and M. N. Petrikova

The V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Acad. Sci. USSR, Moscow

Determination of small amounts of materials by means of well known chemical reactions using ultra-micro-techniques is made possible by maintaining normal concentrations of the reagents, which are achieved by cutting down on the volume of solution used. This leads to an increase (by comparison with macro-methods) of the relative surface of solution and reaction vessel, i.e., to an increase in the surface of unit volume, so that surface is cut down to a smaller extent than the volume. As a result of this factor, certain phenomena which are connected with the existence of a large contact surface between solution and the glass walls of the containing vessel, and the use of capillaries as reaction vessels, acquire particular importance [1]. These phenomena may be prevented, to a considerable extent, if the walls of the micro-flasks are covered with a layer of a silico-organic compound [2, 3].

We made the glass surfaces of the capillaries used hydrophobic by treating the carefully cleaned surfaces with a 3% solution of methylchlorosilane ($CH_3SiCl_3$) in carbon tetrachloride, after which they were heated at 120-130° for one hour. The films obtained in this way are stable to the action of aqueous salt solutions and dilute acids, but less stable to alkaline solutions. The results of such stability tests are given in Table 1.

TABLE 1

Stability of the Hydrophobic Films (at constant temperature)

| Concentration of solutions in N | Time in hours | | | |
|---|---|---|---|---|
| | HCl | $HNO_3$ | $H_2SO_4$ | NaOH |
| 0.1 | >15 | >15 | >15 | 2 |
| 0.5 | 15 | 2.5 | 15 | 1 |
| 1.0 | 3 | 1.5 | 1.5 | 0.5 |
| 3.0 | 1 | 1 | 1 | 0.25 |
| 6.0 | 0.5 | 0.5 | 0.5 | – |

A glass surface covered with a film of methylchlorosilane is not wetted by aqueous solution, so that it is possible to manipulate such liquids without having to rinse out flasks in which they have been used. Using a solution of $Co(NO_3)_2$, with marked $Co^{60}$, and measuring the γ-radiation of wash water and flask, it was found that even with the most careful emptying of a micro-flask, 0.5-2% of solution still remained on the walls. When however, a flask whose walls had been made hydrophobic was used, this was not observed. Titration errors usually connected with the rate of evacuation of solutions from a horizontal buret [4] are also reduced to zero in flasks whose walls have been similarly treated.

Tips of micro-pipets which have been treated with methyl chlorosilane have the big advantage that precipitates formed during a reaction are not deposited on them; moreover, mixing, which is essential during washing of a precipitate, and which is usually done in ultra-micro-analysis by means of the tip of a pipet, does not result in loss of precipitate because of sticking. It should be noted also that precipitates, e.g., sulfides, which are precipitated in micro-apparatus which has been made hydrophobic are easily collected during centrifuging into the conical part of the tube without smearing the walls. Creeping of precipitates of metallo-organic compounds, which is well known to the analyst, e.g., creeping of nickel dimethylglyoxime, is not observed in flasks with treated walls.

The poor wettability of hydrophobic surfaces by aqueous solutions is the result of a reduction in surface tension on the boundary of such surfaces with the solution. Thus, such phenomena as the creep of salts on the outer walls of capillary tubes, and also of calomel micro-electrodes, is prevented by making them hydrophobic. The photographs in Fig. 1 demonstrate this graphically.

A decrease in surface tension as a result of treating a glass surface with methylchlorosilane does not negatively affect the stability with which solutions are held in a capillary tube fixed horizontally. Loss of solution from such a micro-tube as a result of spillage only occurs as a result of energetic shaking. On the other hand, aqueous solutions will not rise spontaneously from a wider tube into a capillary treated with the silico-organic compound. In this connection, it should be noted that when one is dealing with a buret which has been treated, and which is being manipulated with a levelling set-up [5], it is necessary to have a considerably bigger difference in levels than usual in order to get the solution into the buret.

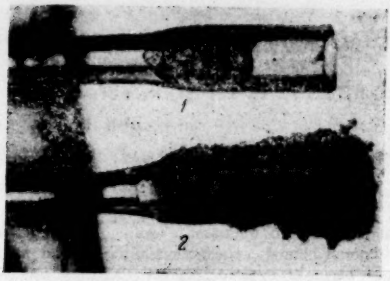



Fig. 1. Micro tubes after evaporation of $NH_3NO_3$ solution
1) Tube treated with methylchlorosilane;
2) untreated tube.

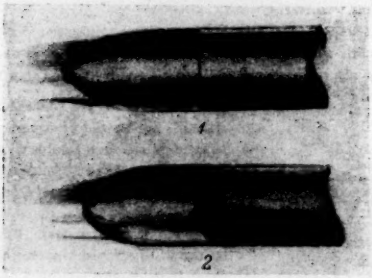



Fig. 2. Shape of the meniscus in a micro tube.
1) Tube treated with methylchlorosilane; 2) untreated tube.

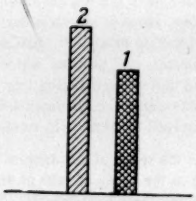



Fig. 3. Rate of evaporation from micro flaks;
1) from a flask treated with methylchlorosilane;
2) from an untreated flask.

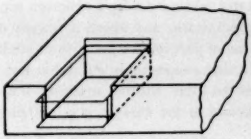


Fig. 4. Dismountable micro flask.

Mention must also be made of the fact that a silico-organic film successfully replaces paraffin on a condenser rod [6].

We have considered in detail before [1], the question of the effect of the curvature of the liquid surface in capillaries and the rate of evaporation of liquids from them.

The free surface of a liquid in a capillary tube treated with a solution of silico-organic compounds, is essentially cut down as a result of straightening of the meniscus (the contact angle on a treated surface is 90-110°, while that on a normal glass surface is 0°), as can be seen from Fig. 2. As a result, the rate of evaporation (from such tubes) is cut down appreciably. Fig. 3 illustrates the comparative evaporation rate under identical conditions from a flat and curved meniscus.

In addition, it is much easier and more accurate to read volumes in burets and flasks visually when the meniscus is flat, since only one clearly defined meniscus line is visible. This is particularly important when dealing with colored solutions.

It is known that there is an exchange reaction between ions in solution and a glass surface. The greater the ratio of surface to volume, the greater the loss of material as a result of its adsorption on the glass walls, particularly from dilute solution [7]. The high ratio of S/V in ultra-micro methods [1], compels one to pay special attention to the possibility of such a loss even from solutions of normal concentrations. This interaction between glass and solution can be prevented by covering the glass walls with a hydrophobic film. Tests carried out show that by working with treated apparatus, loss of material as a result of adsorption decreases appreciably. The use of marked atoms for a study of adsorption [8], made it possible to get rapid and reliable results.

Experiments were carried out with RaE and $Ag^{110}$ in solutions of varying acidity. In order that it should be possible to have direct control of the surface interacting with test material, and at the same time maintain the S/V ratio of a micro-method, we used dismountable micro-flasks, the walls of which were cut from cover glass and were placed in hollows in a mold of plexiglas 2 x 1 x 3 mm (Fig. 4). The glass walls were first carefully cleaned of fat and soap by means of alcoholic alkali; they were then rinsed with distilled water and some of the walls treated with a solution of methylchlorosilane as described above. Into one of these hollows were placed walls which were wettable by water and into another, walls which had been treated with the silico-organic compound. By means of a micro-pipet, equal volumes of the same solution were introduced into the vessels thus made, after which the plexiglas mold was placed in a humidity cabinet, where the solutions were kept for a definite length of time. Solutions and wash water were then transferred from the micro-flasks onto targets for measuring the activity; the micro-flasks were then taken apart, the walls carefully washed with distilled water and this added to the wash liquor. The walls were dried by touching them with the corner of a piece of filter paper, and then placed on an object glass, which served as a support while measuring the activity. Some tests were carried out so that flasks were made from both treated and untreated walls simultaneously, and the difference in adsorption per unit area calculated.

Table 2 contains the results on adsorption of RaE and $Ag^+$ by the walls of the micro-flasks.

TABLE 2

Adsorption of RaE and Ag ions by microflask walls, $\frac{S}{V} = 15$

| Element | Concentration of element in mg/ml | $HNO_3$ concentration in N | Time of contact in hours | Total activity of solution and wash liquors impulses/minute | | Activity of vessel walls, impulses/minute | | Adsorption % | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | I • | II • | I | II | I | II |
| | | 0.1 | 1 | 7050 | 7300 | 980 | 160 | 14 | 2.2 |
| | | 0.1 | 1 | 4200 | 3070 | 670 | 108 | 17 | 3.5 |
| | | 0.1 | 22 | – | 2900 | – | 130 | – | 4.5 |
| RaE | $10^{-14}$ | 0.1 | 20 | 5300 | 6000 | 795 | 455 | 15 | 7.6 |
| | | 0.5 | 2/3 | 7950 | 8600 | 48 | 23 | 0.6 | 0.27 |
| | | 0.5 | 2 | 975 | 1100 | 33 | 18 | 3.4 | 1.65 |
| | | 0.3 | 3.5 | 675 | 690 | 27 | 13 | 4.0 | 1.85 |
| Ag | 80 | 0.001 | 2/3 | 1063 | 915 | 81 | 32 | 7.6 | 3.5 |

• I - untreated flask; II - flask treated with silicon-organic compound.

These results show that adsorption on treated surfaces is one half, one third, one fifth, and even one seventh that on untreated surfaces. The less acid the solution the greater the difference between treated and untreated surfaces. In order, therefore, to get optimum results when using vessels which have been made hydrophobic, it is necessary to work with neutral aqueous solutions. This is an important advantage, since adsorption is not serious in strongly acid solution even when working with untreated flasks.

## SUMMARY

It has been shown that by using silico-organic films in ultra-micro-analysis, it is possible:

1) to do away with the necessity of rinsing out apparatus;

2) to stir up a precipitate with the tip of a pipet without risking loss because of adherence of precipitate to the tip;

3) to reduce titration errors connected with the outflow rate of a solution from a horizontal buret to zero;

4) to prevent creep of salts on to the outer surfaces of apparatus;

5) to lower the evaporation rate from small volumes by straightening the meniscus;

6) to increase the accuracy of measuring solutions in capillaries;

7) to cut down losses of material on the walls of apparatus as a result of adsorption.

It is probable that the technique of making glass apparatus hydrophobic will find wide application in micro-and ultra-micro-analysis.

Received February 24, 1955

## LITERATURE CITED

[1] I. P. Alimarin and M. N. Petrikova, J. Anal. Chem. 7, 341 (1952). (T. p. 377) *

[2] K. A. Andrianov and M. V. Sobolevsky, "High Molecular Weight Silico-Organic Compounds", Defense Industry Press (1949).

[3] M. G. Voronkov and B. N. Dolgov, Nature, USSR, 5, 22 (1954).

[4] I. M. Korenman "Quantitative Micro-Chemical Analysis", State Chem. Press 1949.

[5] I. P. Alimarin and M. N. Petrikova, J. Anal. Chem. 9, 127 (1954). (T. p. 143)*

[6] A. A. Benedetti-Pikhler, "Technique of Inorganic Micro-Analysis" Foreign Lit. Press, Moscow, 1951.

[7] I. Schoovener, J. Research Nat. Bur. Standards 15, 377 (1935).

[8] J. Hensley, A. Long, J. Willard, Ind. Eng. Chem. 41, 1415 (1949).

* T. p. = C. B. Translation pagination.

# A RAPID MASS SPECTROMETRIC MICRO-METHOD FOR ISOTOPIC ANALYSIS OF OXYGEN IN WATER

A. I. Brodsky, S. G. Demidenko, L. L. Strizhak, and V. R. Lechekhleb

The L. V. Pisarzhevsky Institute of Physical Chemistry, Acad. Sci., USSR, Kiev

Mass spectrometric determination of the $O^{18}$ content of water is best carried out by measuring the mass peaks 44 and 46 in $CO_2$ after exchange of the latter with test water.

The methods usually recommended [1], require water in amounts of 1 g, a prolonged exchange time, and control of temperature on which the exchange equilibrium depends. Trofimov's method [2], which he suggested recently, and in which exchange is made with dissolved carbonate at the boiling point, is free from these drawbacks; but even this method requires 0.5-1 g and the additional operations of separating the solid salt from solution, and decomposition of the carbonate after the exchange.

We have developed a rapid method which requires 20 mg of water,* and which is no less accurate than the macro-method; it is a variant of a method described briefly by Dostrovsky and Klein [3], and is based on exchange of $CO_2$ with the vapor of the test water over a glowing platinum wire. We are convinced that this method is reliable and is easy to carry out because we have used it for a long time for current isotopic analysis of oxygen.

## Method

The exchange apparatus which is identical with that described in [3], is shown in Figure 1. Exchange is carried out in flask A with a volume of 100 $cm^3$, into which is led 25 cm of 0.2 mm platinum wire in the form of three loops. Flask A is fused as closely as possible to the stopcock C and the bottom of one of the platinum loops is fitted close to this junction of A with C. Unless these precautions are taken reproducible results cannot be obtained because of dilution of the aliquot of test water by residual condensate from previous analyses. Pure $CO_2$ was obtained by heating sodium bicarbonate to 400° in flask H. The mixture of $CO_2$ and $H_2O$ was frozen with liquid air in trap I. After substituting the liquid air by a mixture of dry ice and acetone, the dry $CO_2$ was evaporated into the supply reservoir L under pressure, approximately atmospheric. For a volume of 1/3 liter for L, the supply of $CO_2$ is sufficient for several dozen analyses.

The dose of test sample —20 mg water — is introduced by means of a micro-pipet into E (the dosage cavity of the stopcock D), and is then frozen by placing flask M filled with liquid air under it. Liquid air is also poured into the hollow B of flask A. F is then closed, tap C opened, and D rotated so that the dosing cavity comes opposite its right socket. The cavity is carefully warmed with a small electric heater, so that the water which evaporates condenses on the cold wall of flask A; C is then closed. The dose of $CO_2$ is then let out of the reservoir L into the recess between taps C, D, and F (ca. 30 $cm^3$, at a pressure of 40 mm); tap C is opened and the $CO_2$ condenses on the same cold wall of flask A. Tap C is now closed again, the liquid air is removed from B and the current is gradually turned on, bringing the temperature up to 1100° or higher. After evaporation of the mixture of $CO_2$ and $H_2O$, exchange is complete in less than 5 minutes. Preliminary freezing of the water before turning tap D is essential for accurate analysis, since liquid water spatters and wets the ground glass joint. When exchange is complete, taps C and F are opened and the equilibrium mixture of $CO_2$ and $H_2O$ is transferred into flask K which has a volume of ca. 100 $cm^3$. The apparatus is then ready for the next analysis. All these operations are carried out after all the apparatus has been carefully evacuated with a mercury pump.

Flask K is transferred to the entry tube of a mass spectrometer which is shown in Fig. 2. Water from the mixture of $CO_2$ + $H_2O$ is frozen in tube A, while the dry $CO_2$ is let into tube B under a pressure of 25-30 mm, from which it is pumped over into reservoir D with a pump C. Gas is let into the inonizing chamber H of the mass spectrometer through diaphragm F made of platinized tin with an opening of 0.05 mm, fused into the upper part of the internal tube of vessel E. A piece of gold foil G is used to hold back any mercury vapor. In order to get reproducible results and to decrease the background in the mass spectrometer, it is essential to wire valve E and its connection to H with heating wire in an asbestos lining in order to heat the system for 30 minutes before a series of analyses.

* This amount of water can be cut down considerably with some sacrifice of accuracy.

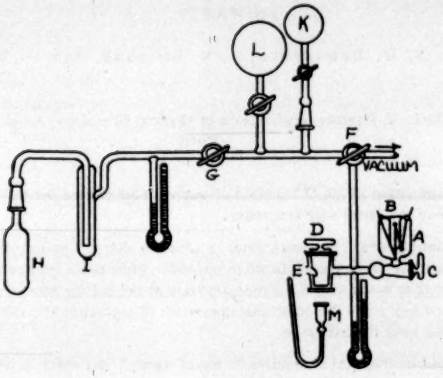



Fig. 1

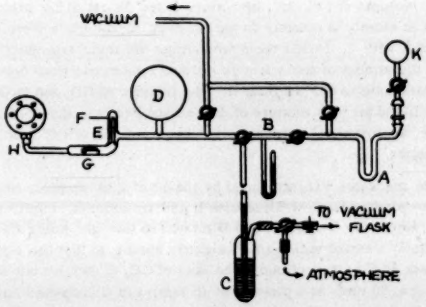



Fig. 2

We used a MS-2 mass spectrometer. With a volume of 600 $cm^3$ for D and a pressure of 0.1 mm, it was possible, in the course of 30-40 minutes to get a stable mass peak of 44 with a height of $6\text{-}10 \cdot 10^3$ mV. Under these conditions, after a small correction for background, the ratio R of the peaks 46 and 44 could be measured with an accuracy of up to 1%.

For a series of determinations, one analysis, including mass spectrometric measurements took 40-50 minutes.

## Equations used for Calculation

The equations given [1, 2, 3] for calculating the $O^{18}$ content of water from the height of the 44 and 46 peaks in $CO_2$ after exchange, do not take into account the contents of $O^{16}$ and $O^{18}$ in molecules of $CO^{16}$ $O^{17}$ and

$CO^{17}O^{18}$, which also participate in the exchange, so that an error is introduced which increases in proportion with $O^{18}$ content and amounts to 2% for 10% $H_2O^{18}$*. The equations given below include a correction for this factor.

During the exchange between $CO_2$ and $H_2O$ the following equilibriums are established:

$$H_2O^{17} + CO^{16}O^{16} = H_2O^{16} + CO^{16}O^{17};\ K_1 = 1/2$$
$$H_2O^{18} + CO^{16}O^{16} = H_2O^{16} + CO^{16}O^{18};\ K_2 = 1/2$$

and three of the following type:

$$CO^{16}O^{16} + CO^{18}O^{18} = 2CO^{16}O^{18};\ K_3 = 4$$

The limiting values indicated for the equilibrium constant are known to be reached even at T = 1000° K [4], so that a control of the temperature of the platinum wire is unnecessary.

For these values of the constants, a statistical distribution of the isotopes occurs[5], and the concentrations are equal to:

$$[CO^{16}O^{16}] = (1-u-v)^2;\ [CO^{16}O^{17}] = 2v(1-u-v);$$
$$[CO^{16}O^{18}] = 2u(1-u-v);$$
$$[H_2O^{16}] = 1-m-n;\ [H_2O^{17}] = n;\ [H_2O^{18}] = m,$$

where m, n are the atomic fractions of $O^{18}$, and $O^{17}$ in water, and u, v are the respective atomic fractions of $O^{18}$ and $O^{17}$ in $CO_2$ after exchange. These values before the exchange, are designated by $m_0$, $n_0$ (in $CO_2$ analyzed) and $u_0$, $v_0$ (in the natural $CO_2$ and water). In a state of exchange equilibrium, for these values of the constants, we have:

$$m = u \text{ and } n = v. \tag{1}$$

If a moles of water and b moles $CO_2$ are taken for exchange, where 2b/a = A, then the balance of $O^{18}$ and $O^{17}$ gives:

$$m_0 = M + A(u-u_0) \text{ and } n_0 = n + A(v-v_0). \tag{2}$$

The ratio of heights of the mass peaks 46 and 44** is given by:

$$R = \frac{[CO^{16}O^{18}]}{[CO^{16}O^{16}]} = \frac{2u}{1-u-v}. \tag{3}$$

Simultaneous solution of equations (1), (2), and (3), gives

$$m_0 = (1+A)\cdot\frac{R}{2+(1+p)R} - Au_0, \tag{4}$$

where p = n/m. Assuming the ratio $O^{17}/O^{18}$ to be constant, i.e., $p = p_0 = v_0/u_0$ (as in natural water), and according to the most reliable results [6], $u_0 = 1/489$ and $p_0 = 0.18$, we finally get:

$$m_0 = (1+A)\frac{R}{2+1.18R} - 0.002039A. \tag{5}$$

According to experimental conditions the value of A can be very accurately determined. In the apparatus described A = 0.04-0.1 so that it is sufficient to dose the water and $CO_2$ approximately.

More exact calculation of $m_0$ requires a knowledge of the true value of the ratio $O^{17}/O^{18}$ in the test. This can, in principle, be determined by measuring the height of the mass peak 45:

$$R' = \frac{[C^{12}O^{16}O^{17}] + [C^{13}O^{16}O^{16}]}{[C^{12}O^{16}O^{16}]} = \frac{2v}{1-u-v} + 0.0111,$$

where it is assumed that $C^{13}/C^{12} = 0.00111$ [6]. Then $p = (R'-0.0111)/R$. The difference $R'-0.0111$, can, however, only be determined reliably in strongly enriched water. On the other hand, the error for an incorrect value of p is not large. If the error in p is 100%, the error in $m_0$ is 0.2% for 1% $H_2O^{18}$ and 2% for 10% $H_2O^{18}$. Consequently, equation [4] can only be used in conjunction with additional measurements of the height of peak R', instead of simplified equation (5) in the case of strongly enriched heavy oxygen water.

---

* Here and elsewhere it is assumed that $H_2O^{18}$ contains an amount of $H_2O^{17}$ corresponding to the natural ratio of $O^{18}/O^{17} = 5$.

** To simplify calculation we ignore the fraction of $C^{12}O^{17}O^{17}$ and $C^{13}O^{16}O^{17}$ in the 46 peak. This leads to an error of 1% only for 50% $H_2O^{18}$ or 10% $H_2O^{17}$.

## Comparison with Densimetric Analysis

Correlation of mass spectrometric and densimetric analysis is of essential practical importance. The accuracy of a carefully carried out flotation analysis [5], is commensurable with that of mass spectrometric analysis for an excess density of $H_2O^{18}$ greater than 100-200 γ units.

At low concentration, for small changes in the isotopic composition, the first method is more accurate. In a number of cases, therefore, it is expedient to combine the two methods. On the other hand, a comparison of both methods allows one to check on the correction of the coefficients used for converting from excess density Δd to atomic fraction $m_0$ of the $O^{18}$ isotope in water.

If, for pure $H_2O^{18}$ and $H_2O^{16}$ the densities are $d_{18}$ and $d_{16}$, while $d_{18}/d_{16} - 1 = B$, then for pure $H_2O^{17}$ and $H_2O^{16}$ it is possible, with sufficient accuracy, to assume that $d_{17}/d_{16} - 1 = B/2$. The simple calculation based on the additivity of molar volumes of isotopic mixtures, gives

$$\Delta d = \frac{B}{2 + B(2 + p_0)u_0} \cdot [(2 + p)m_0 - (2 + p_0)u_0], \qquad (6)$$

where Δd is the excess density above that for natural water. Hitherto, no data have been published on the densities of pure $H_2O^{18}$ and $H_2O^{17}$ and it is arbitrarily assumed on the basis of the approximate equality of the molecular volumes of the isotopes that $B = 20/18 - 1$. Then for $p = p_0 = 0.18$:

$$\Delta d = 121080\, m_0 - 247.1 \text{ γ units} \qquad (7)$$

Equations (5) and (7) permit comparison of the $O^{18}$ contents, determined mass spectrometrically and densimetrically.

When the value of p in the expression $O^{17}/O^{18}$ is given incorrectly, this error has a markedly lesser effect upon mass spectrometric analysis than upon flotation analysis; when the absolute error is $\delta p$ we obtain the value of p in $\delta m_0/m_0$ by means of Formula (7) $\delta p/2$ or approximately by means of Formula (4) $m_0 \delta p$. Thus the error in the case of mass spectrometric analysis is less by the numerator $2m_0$. This is one of the essential advantages of the mass spectrometric method.

## Checking the Method

A sample of heavy-oxygen water was completely freed from excess deuterium by blowing $NH_3$ through it. It was then electrolyzed twice. From this and from standard river water, test samples were prepared by dilution by weight. Each of the four samples was repeatedly analyzed by three methods:

1) by an ordinary flotation method [5], for which 3-5 g was taken:

2) by a micro-flotation method using a Gilfilyan float without a membrane; the float was controlled by adjusting temperature and not pressure*; 30-50 mg of water was required.

3) by the mass spectrometric method just described using 20 mg water. Mass spectrometric analysis of the tests were alternated with analysis of standard water. For the latter, we got, on different days, values of $R_0$ varying from 0.00403 to 0.00410 (instead of the tabulated value of $R'_0 = 0.00409$), which amounts to a correction of from 4 to 0 γ units.** On the basis of the macro-flotation analysis, we accepted the value $\Delta d = 1068$ γ, for the original water. The micro-float was calibrated on the basis of this value.

The table contains results of several independent analyses of each of the test samples by the three methods. For an accuracy of determination of R of ca. 1% and of $R_0$ of ca. 2%, the expected accuracy of the mass spectrometric method amounted to ca. $5 + 0.01\Delta d$, γ units, which is in agreement with published results.

Comparison of densimetric and mass spectrometric results permits one to draw conclusions of practical importance for isotopic analysis of water; viz, that the coefficient used for calculation, $B = 0.1111$ [5], for which no data on the density of pure $H_2O^{18}$ are available for its experimental determination, differs from the true value by not more than 2%.

We wish to thank A. S. Fomenko, I. P. Gragerova and T. M. Abramov for carrying out densimetric analyses, and I. S. Volnenko for his help in assembling the mass spectrometer.

* This method was developed by I. P. Gragerov and is described in a separate article.

** In order to eliminate the systematic apparatus error in formula (5), it is necessary to substitute $\frac{R_0}{2 + 1.18\, R_0}$ instead of the tabulated value of $\frac{R'_0}{2 + 1.18\, R'_0} = 0.002039$.

Comparison of the analytical results.

| Number of test | Excess density of water in γ units | | | |
|---|---|---|---|---|
| | calculated from dilution | by the flotation method | by the micro-flotation method | by the mass spectrometric method |
| I | (1068) | 1069, 1067<br>1069 | 1066, 1070<br>1068 | 1069, 1068, 1083, 1076, 1065, 1065 |
| | | | | Average 1071 |
| II | 753 | 754, 753 | 756, 747 | 755, 760, 755, 752, 751 |
| | | | | Average 755 |
| III | 527 | 523, 522 | 519, 525 | 525, 525, 535, 530 |
| | | | | Average 529 |
| IV | 261 | 259, 258 | 254, 254 | 266, 267, 269, 265, 259, 265 |
| | | | | Average 265 |

## SUMMARY


1. A mass spectrometric method is proposed for determining the isotopic composition of oxygen in water, which requires 20 mg water. An analysis takes 40-50 minutes and has an accuracy of ca. 1-2% for water with an excess density of 300 γ units.

2. Equations which can be used for calculating the results are given for the method, and also for comparing it with a densimetric method taking into account the $O^{17}$ content.

3. It has been shown that the normally accepted value of the coefficient used for determining the atomic fractions of $O^{18}$ from densimetric measurements does not differ from the true value by more than 2%.



Received December 18, 1954


## LITERATURE CITED


[1] I. Kirshenbaum, "Physical Properties and Analysis of Heavy Water," Foreign Literature Press, (1953).

[2] A. V. Trofimov, J. Anal. Chem., 8, 353 (1943).

[3] I. Dostrovsky, F. S. Klein, Anal. Chem., 24, 414 (1952).

[4] H. C. Urey, J. Chem. Soc., 1947, 562; "Chemistry of Isotopes", Chapter 1, p. 86 (1948).

[5] A. I. Brodsky, "Chemistry of Isotopes", Acad. Sci. USSR Press, (1952).

[6] A. Nier, Phys. Rev., 77, 789 (1950).

BLANK
PAGE

## BRIEF COMMUNICATIONS

# A CELL FOR QUANTITATIVE INFRARED SPECTRAL ANALYSIS, AND AN APPARATUS FOR MEASURING THE THICKNESS AND THE WEDGE OF CELLS

I. V. Berezin and G. B. Meluzova

The M. V. Lomonosov Moscow State University, Chemistry Faculty

Cells which are used for spectral analyses in the infrared are usually made from such materials as potassium bromide, sodium chloride, potassium chloride, and lithium fluoride. As a result of the low mechanical stability of these materials and of their solubility in water and some other solvents, their use for making cells requires considerable care and necessitates working with absolutely dry materials. Nevertheless, even when the greatest care is taken, the salt plates are fairly easily destroyed and require regular repolishing. Polishing is made easier by the use of dismountable cells. All the same current types of such cells suffer from a number of serious drawbacks. In particular, the dismountable cells of the IKS-11 infrared spectrometer require complete dismounting and assembly for each filling with test liquid. Frequent repetition of these operations leads to a fairly rapid break-down of the salt plates. In addition, it is difficult to control the thickness of the liquid layer, which may alter with the force used to press the plates together, and with mechanical deterioration of the lead gaskets.

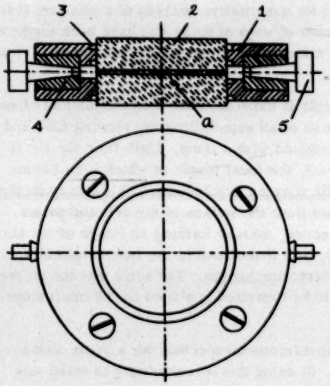



Fig. 1.

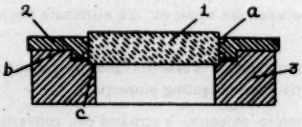



Fig. 2.

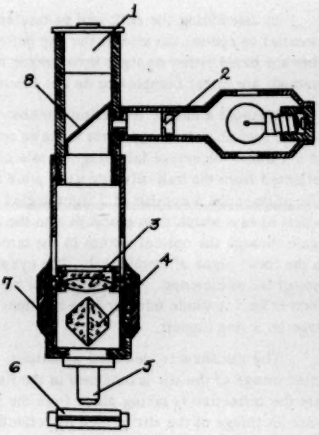



Fig. 3.

The use of dismountable cells with their current construction [1], is also attended by some snags; the difficulty of dismantling and repolishing the salt plates, and difficulty of washing and preventing outflow of test liquid from a fairly large layer thickness. Thus a cell used for spectral analysis in the infrared should meet

the following basic requirements: a) the distance between the salt plates should be capable of easy regulation and remain constant during a whole series of tests; this is particularly important when carrying out quantitative analysis of a mixture of various compounds; b) it should be easy to fill, empty, and wash; no liquid should flow out of the cell at all; c) when mixtures of volatile and non-volatile liquids are being analyzed, no evaporation should occur at all; d) it should be easy to dismantle, and to polish the salt plates.

We have constructed a cell, which, to a considerable extent, satisfies these basic requirements. A cross section of the cell is shown in Fig. 1. It consists of two metallic covers : 1, in which two openings are bored, and with a fairly compact packing along the diameter of the salt windows; 2, along the circumference of the opening, two grooves are made, from both sides, for bracing the windows with silver or copper amalgam 3. (Ready-made dental amalgam is convenient to use).

The salt windows project a little above the surface of the covers so that they can be polished without removing them from their mounting. The cover is braced with screws to ring 4. Lead packing is used between the covers and ring 4. The thickness of the ring and the lead packing is chosen so as to ensure the requisite size for the gap a between the salt windows. Along the diameter of the ring two openings are made, to which are connected conical metallic stoppers 5 (via ground joints). During cell assembly, considerable deviations from the mutually parallel position of the internal surface of the salt windows are possible. To avoid this, the following procedure should be adopted. Salt windows 1 and the cover 2 are laid on the corresponding grooves of the special setting 3 so that, as shown in Fig. 2, groove a is filled with amalgam.

It must be noted that in carrying out this operation both the window and the cover are fairly compactly pressed to the surface of the mounting. Everything is left in this position till the amalgam hardens, when the cover is rotated and the groove is filled with amalgam from the opposite side.

If the end surfaces b and c of the mounting are filled mutually parallel and if the end surfaces of ring 4 (Fig. 1) are also mutually parallel, then the value of the wedge between the window surfaces will remain within the permitted limits. Some difficulties may arise in this case, if a foil is used for packing which is not of uniform thickness. In this case the wedge shape of the gap between the windows may be cut down to some extent by rotating the gaskets relative to each other.

In assembling the cell, and particularly in preparing a pair of cells for quantitative analysis of a mixture, it is essential to control the size of the gap between the salt windows. A number of ways of doing this have been suggested. They are based either on light interference or on successive focusing of a microscope on the window surfaces,2. These methods are either complex or do not ensure the necessary accuracy.

We used a double reflection method, which, while being fairly simple is more accurate than the method of successive focusing. The apparatus is shown schematically in Fig. 3; it consists of an autocollimating viewing tube and an 8 x micro-objective fulfilling the role of a collimator. Slit 2 is illuminated with a lamp. Light from the slit is reflected from the half-silvered glass plate 8 and passes through objective 3, the focal length of which is ca.80mm. The prism-cube 4 consists of 2 right angled prisms glued together and with silvered hypotenuses. This also splits the pencil of rays which then proceeds into the micro-objective 5, is reflected from the surface of the cell and passes again through the optical system in the same way but in the opposite direction, thereby forming an image of the slit in the focal plane of eyepiece 1. The eyepiece is a 15 x. The optical system is mounted in the tube holder of a biological microscope. The thickness is measured by means of a micrometer mechanism. The scale division on the drum is 2$\mu$. A whole number of revolutions is read off directly. Cell 6 to be measured is placed on the microscope stage on a ring support.

The thickness is measured as follows: by moving the stage with the micrometer mechanism, a sharp, unbifurcated image of the slit is obtained in the field of vision of the eyepiece. In doing this it is necessary to make sure that the reflection is taking place from the inner surface of one of the windows. Then by shifting the stage up or down an image of the slit formed by reflection of the light from the inner surface of the second window is obtained. The difference in readings of the micrometer gives the size of the gap between the windows. To eliminate backlash, sighting is carried out from one side.

After some practice, an accuracy of $\pm$ 1$\mu$ is possible. During measurements it is essential that the surfaces of the salt windows should be well polished and that they should possess pretty good reflecting properties.

For measuring the wedge, the following procedure is adopted: the micro-objective is screwed out, converting the apparatus thereby into an autocollimating telescope. Having placed a glass plate or mirror on the microscope stage, shifting objective 3, and turning ring 7, a sharp image of the slit is obtained in the field of vision. The cell is then placed on the stage. If the image is not split into two, this means that there is no wedge. Bifurcation of the

image signifies a wedge and its size can be determined by the equation: $\alpha = a/2f$, where $a$ is the distance between the images of the slit which can be measured with the eyepiece micrometer; and $f$ is the focal length of the objective 3. By switching the lead gaskets around or by rotating them with respect to one another, it is possible to get a wedge within the tolerance limits.

Some difficulty in evaluating the wedge shape of the gap is caused by the fact that reflection of the slit not only occurs from the inner surfaces of the windows, but also from the outer surfaces. It is possible therefore to have four and not just two slit images (when the windows form a wedge). In such cases, one can be guided by the intensity of the image. Reflections from the lower surfaces are much less bright.

We have used the cell, and the apparatus for measuring the thickness and wedge shape of the cell, described above, daily, for a long time, and have proved that they are entirely suitable for quantitative spectral analysis in the infrared.

Received October 29, 1954

## LITERATURE CITED

[1] C. Smith, Muller, Elmer, J. Opt. Soc. Am. 34, 130 (1944); Gilbert Kivenson, Albert Roth, Myrtle Rider, J. Opt. Soc. Am. 39, 484 (1949); N. B. Colthup, Rev. Sci. Inst. 18, 64 (1947); J. White, Rev. Sci. Inst. 22, 833 (1951).

[2] V. M. Chulanovsky, "Introduction to Molecular Spectral Analysis", 1951, p. 226; W. A. Wildhach, Rev. Sci. Inst. 18, 803 (1947).

BLANK
PAGE

TRANSLATION TO AND FROM ALL LANGUAGES

by bilingual chemists and engineers:

Rates for translation into English:

| Languages | Price per 1000 words |
|---|---|
| French | $10.00 |
| German | 10.00 |
| Italian | 10.00 |
| Russian | 10.00 |
| Spanish | 10.00 |
| Dutch | 12.00 |
| Other languages | Rates upon request |

CONSULTANTS BUREAU
152 West 42nd Street
New York 18, New York